



# ***Theoretical Studies of High Energy Oxygen Atom Chemistry***

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  - B. Ramu Ramachandran, Louisiana Technical University
  - J. Bowman, T.Xie, Emory University
  - T. Minton, Montana State University



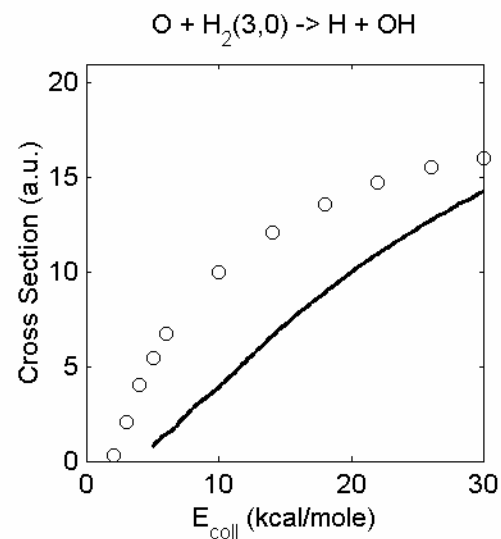
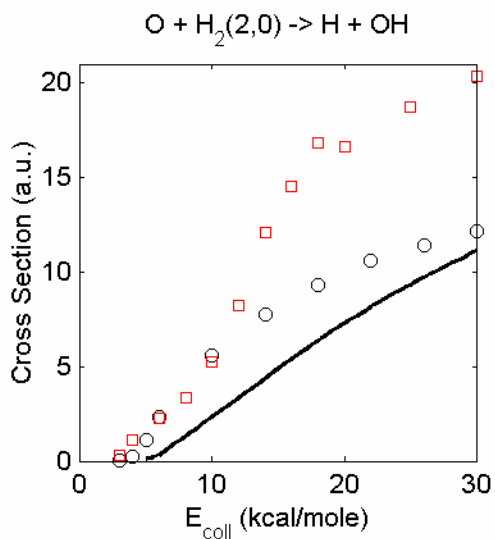
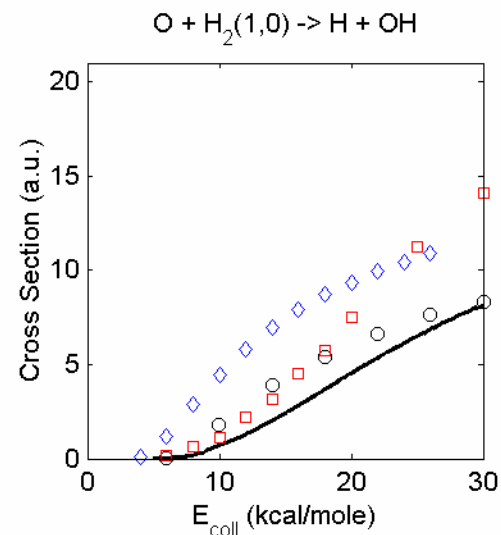
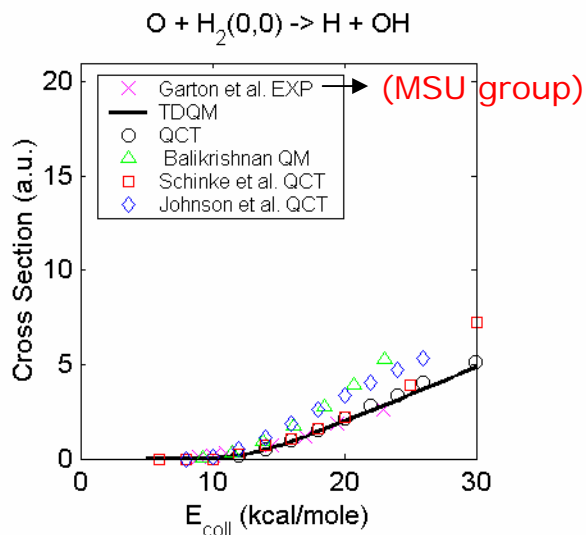
# Outline

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- Ab-initio Modeling of the Following Reactions:
  - $O + H_2 \rightarrow OH + H$
  - $O + H_2O \rightarrow O + H_2O^*, OH^{**} + OH^*$
  - $O + HCl \rightarrow O + HCl^*, Cl + OH^*$

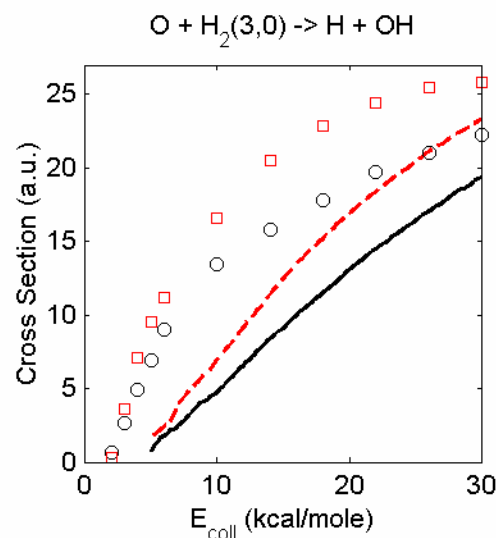
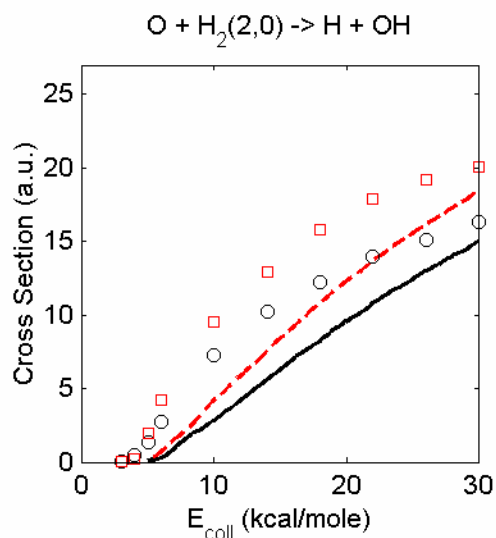
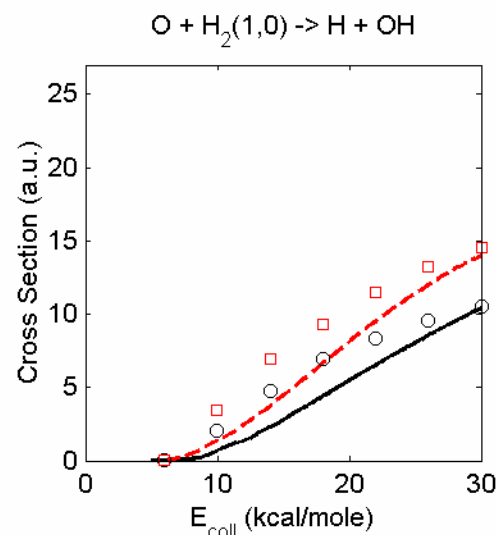
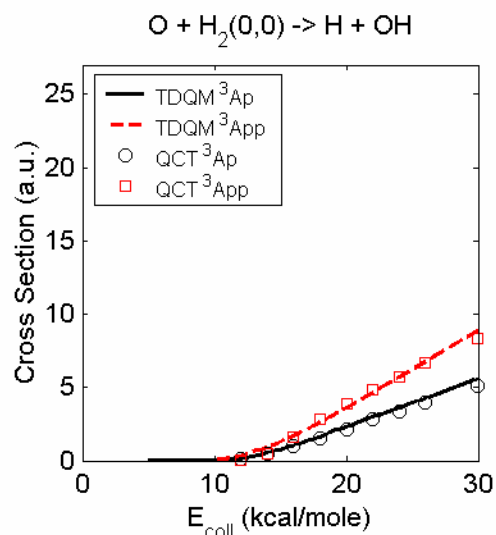


# Cross Sections vs. Energy $H_2(v)$



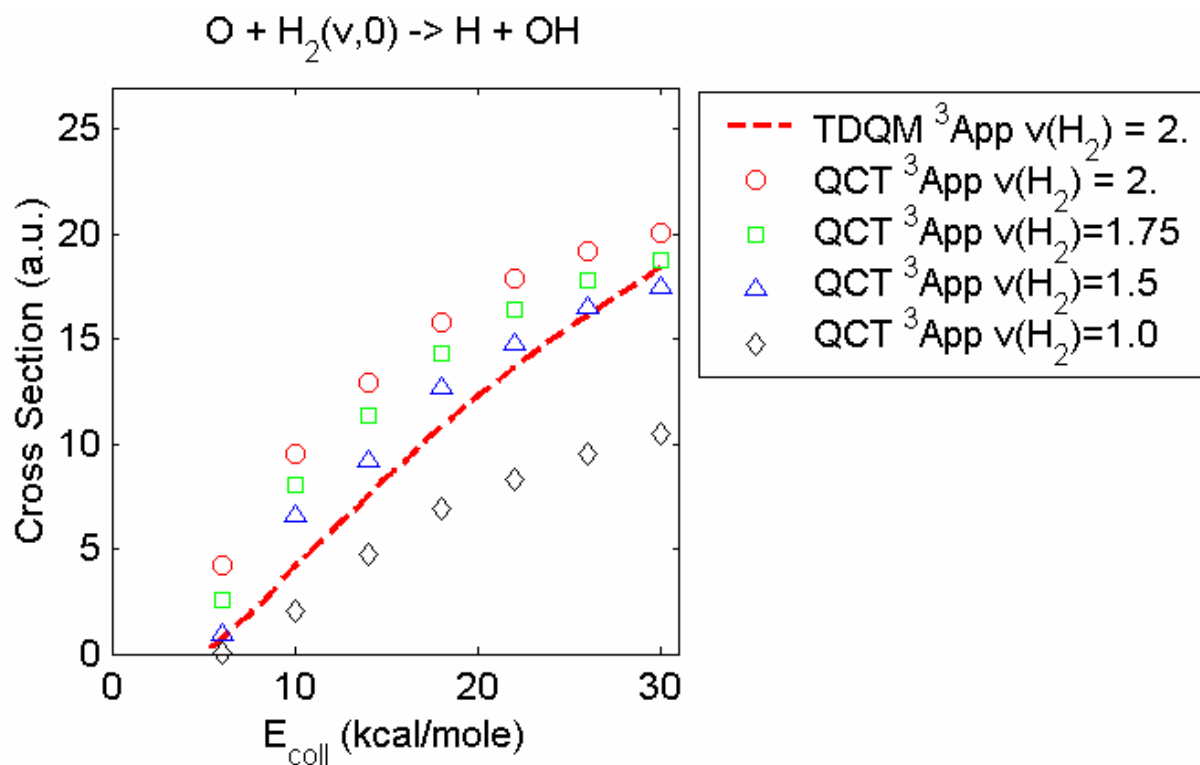


# Comparisons with QM



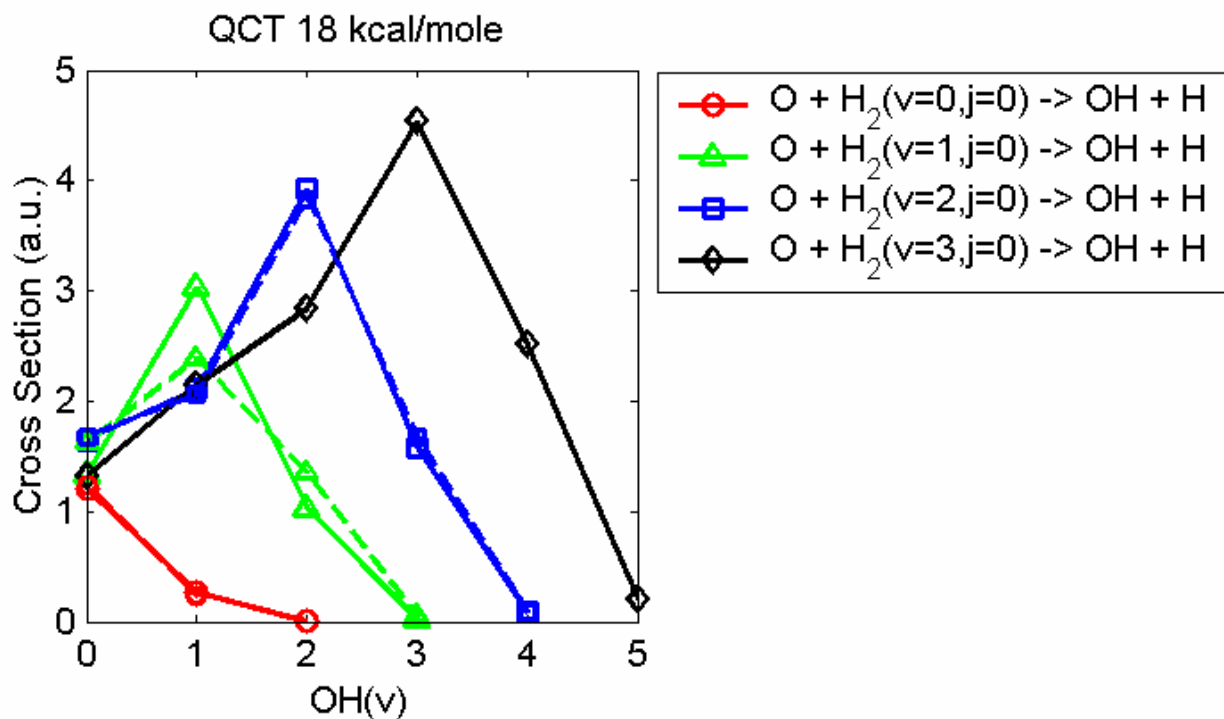


# Adjusting QCT to Match QM





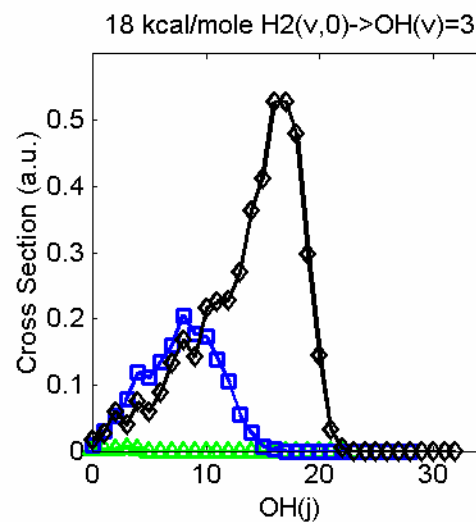
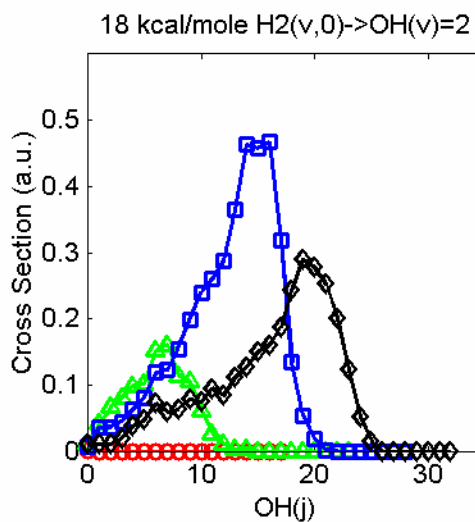
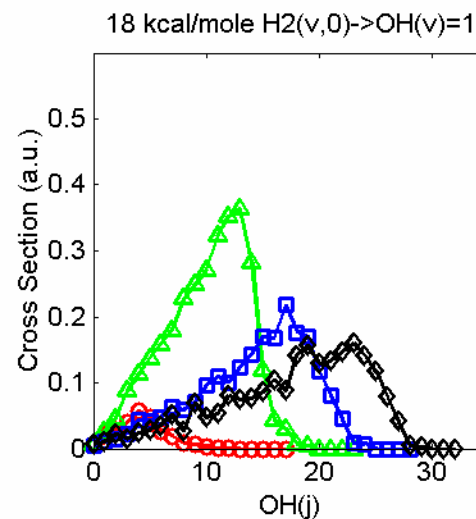
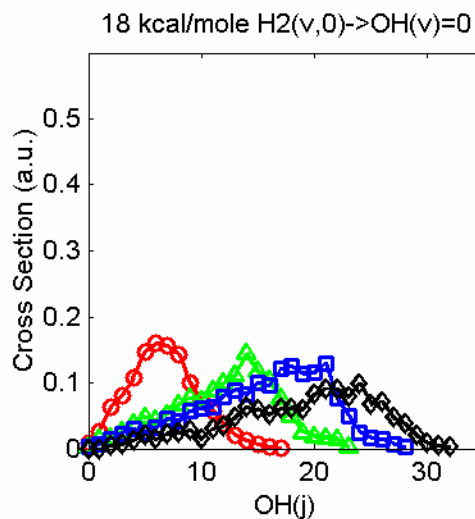
# Vibrational Distributions



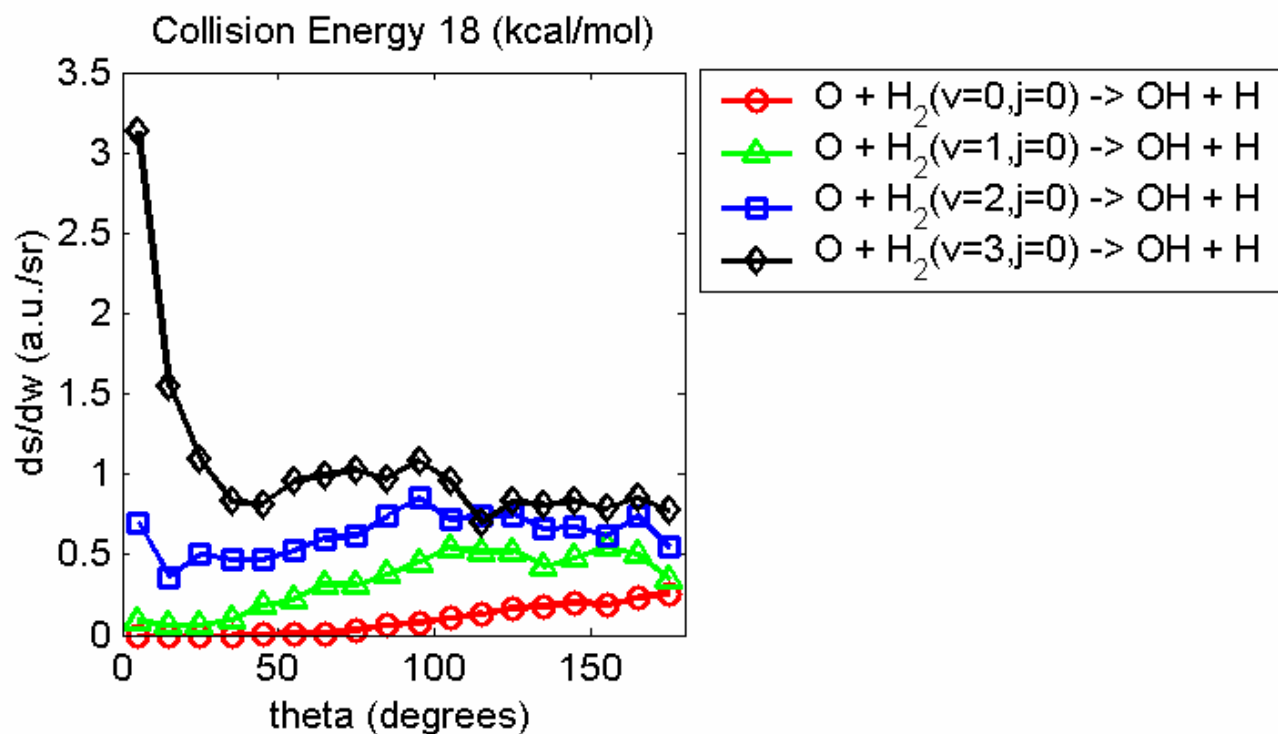




# Rotational Distributions

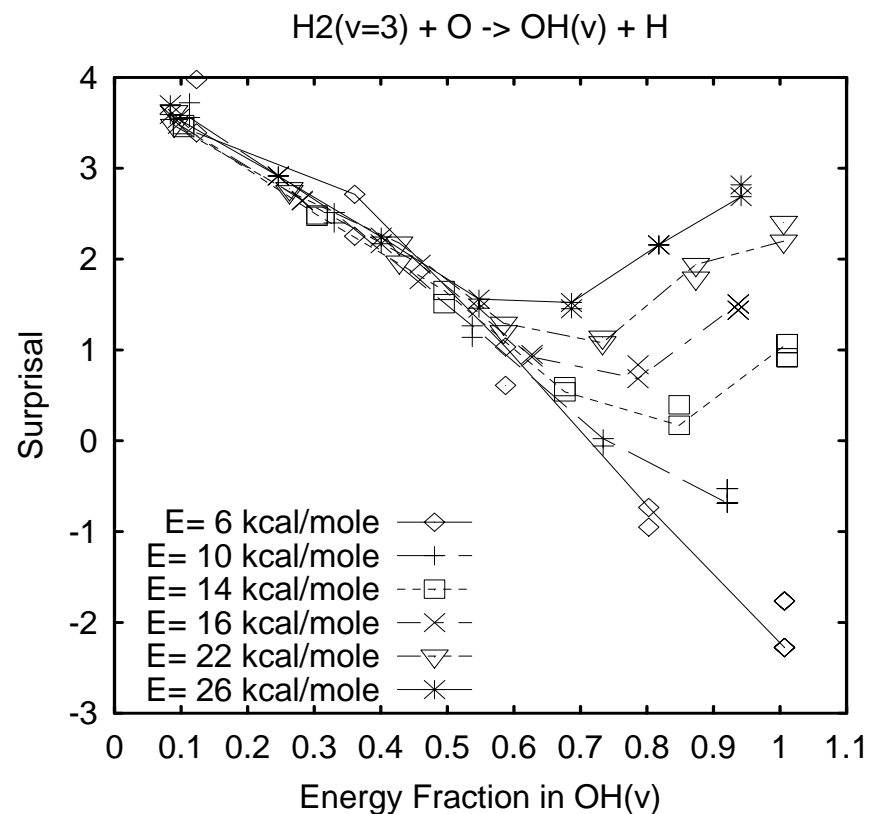
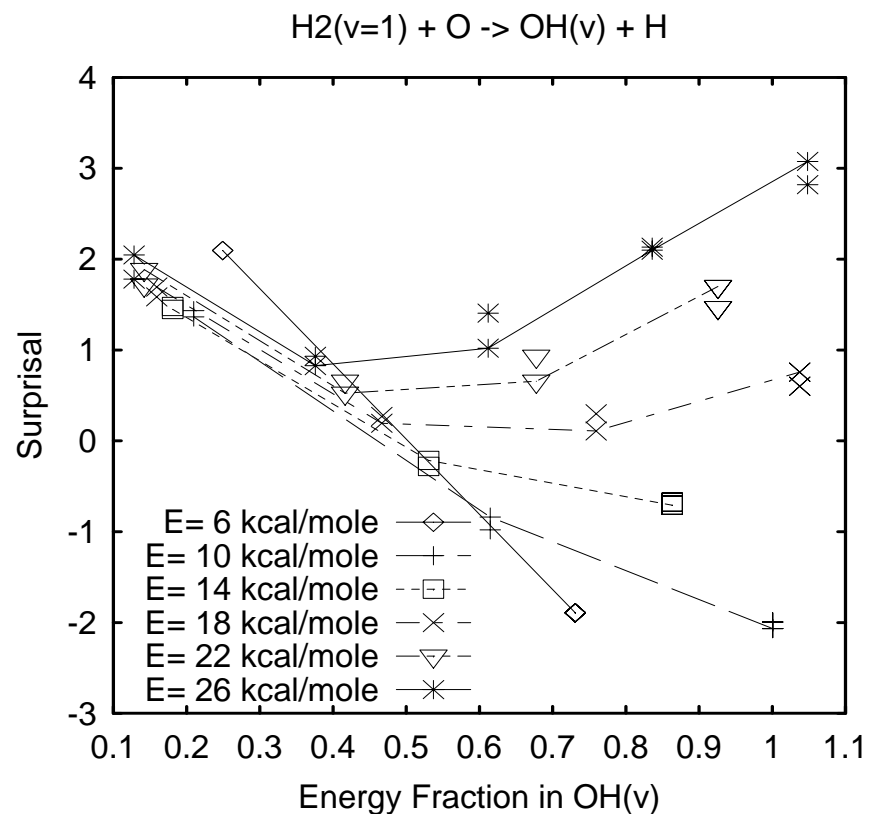


# Angular Distributions



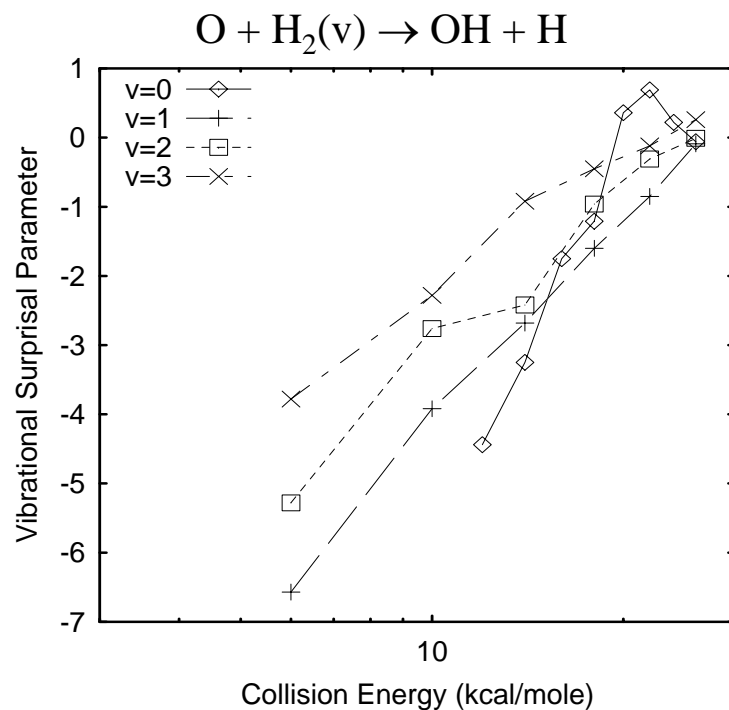


# Surprisal Fits of Vibrational Distributions





# Vibrational Surprisal Parameter vs. Energy





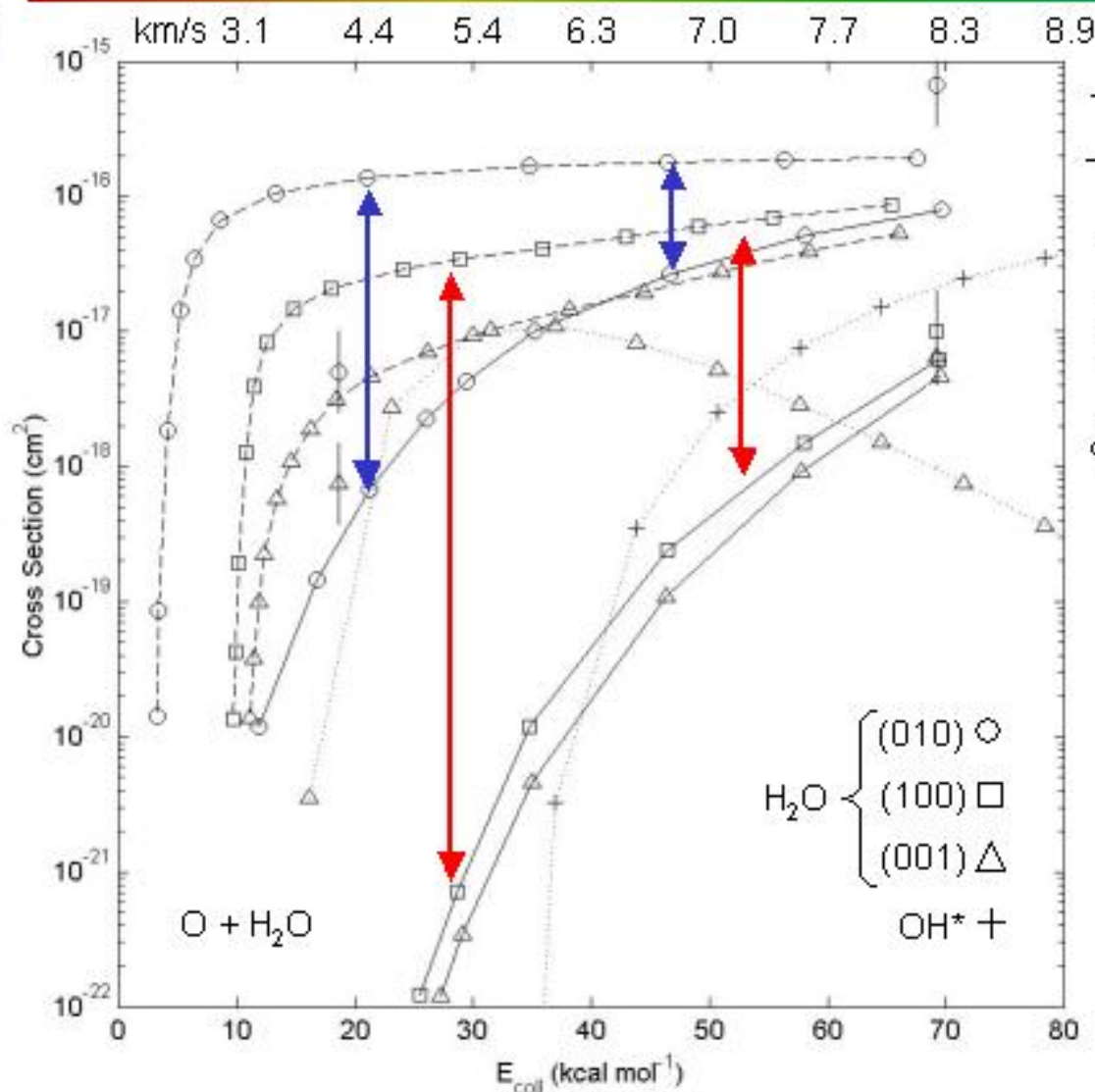
# Overview of the O + H<sub>2</sub>O System

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- Principal channels
  - $\text{O} + \text{H}_2\text{O} \rightarrow \text{O} + \text{H}_2\text{O}^*$
  - $\text{O} + \text{H}_2\text{O} \rightarrow \text{OH}^{**} + \text{OH}^*$
- Experimental Studies
  - Shuttle Observations (~8 km/s)
  - Shock Tube (~4.3 km/s)
  - Physical Sciences Inc. (CVF) measurements (~8 km/s)
  - Rate constants up to ~2500 K
  - Recent measurements
    - $(\text{H}_2\text{O})\text{O}^- + \text{photon} \rightarrow \text{OH}^* + \text{OH}^{**}$  (transition state information)
    - $\text{O} + \text{HOD}(4v_{\text{OH}}) \rightarrow \text{OH}^* + \text{OD}^*$
- Theory
  - Old 'non-reactive' surface
    - Johnson (Quantum)
    - Redmon et al. (Classical)
  - Large disagreements
- Measurements are sparse and Theory not really helpful



# Calculations and Measurements of the O + H<sub>2</sub>O Cross Sections



- Johnson QM-IOS 1986
- - - Redmon et al. QCT 1986
- ..... Bernstein et al. 1996 spectral fit
- △ Dunn et al. 1975 shock tube (low energy)
- □ △ Meyerott et al. 1994 Spacelab 2 (high energy)

Note: Large differences between Theory results



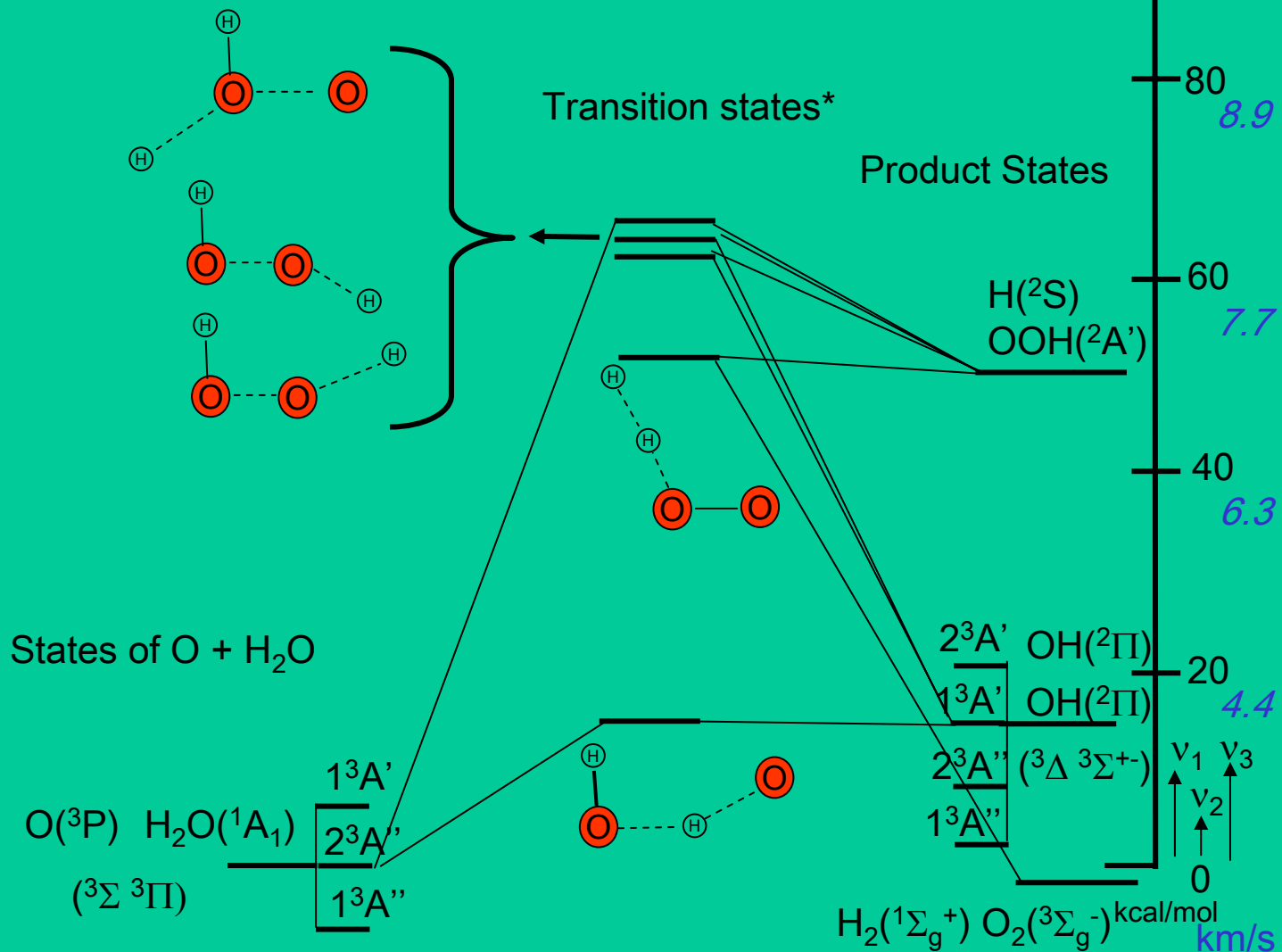
# O + H<sub>2</sub>O Reaction Approach

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- Short Term:
  - Perform direct dynamics calculations with VENUS
    - Quick picture of reaction chemistry (but less accurate)
    - AM1, PM3 level of theory (approximate)
- Long Term:
  - Generate new O + H<sub>2</sub>O surfaces and do reactive scattering calculations
    - Compute new high level *ab-initio* reactive surface
    - Fit surface
    - Run classical trajectory calculations with VENUS

OH( $^2\Sigma^+$ ) OH( $^2\Pi$ )

# Low Adiabatic States for O + H<sub>2</sub>O collisions (TRIPLETS)

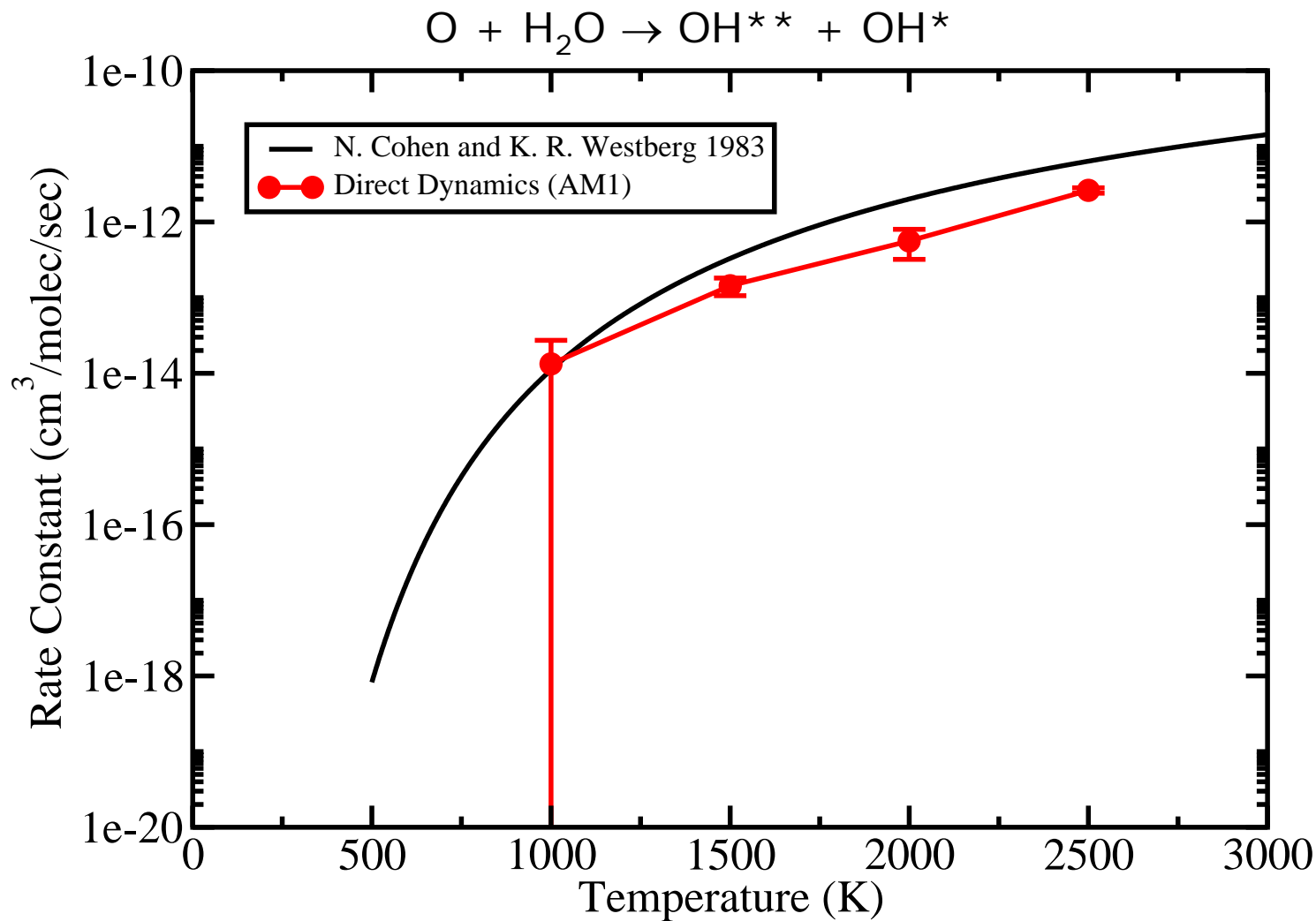


\*Karkach and Osharov, JCP, 110 11918 (1999)



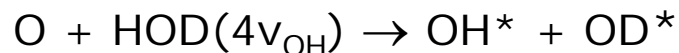


# Reactive Rate Constant:





# HOD\* + O Direct Dynamics Results: Comparisons to Experiment



Pfeiffer *et al.* J. Chem. Phys. Vol. 113, 7982 (2000): Experiment

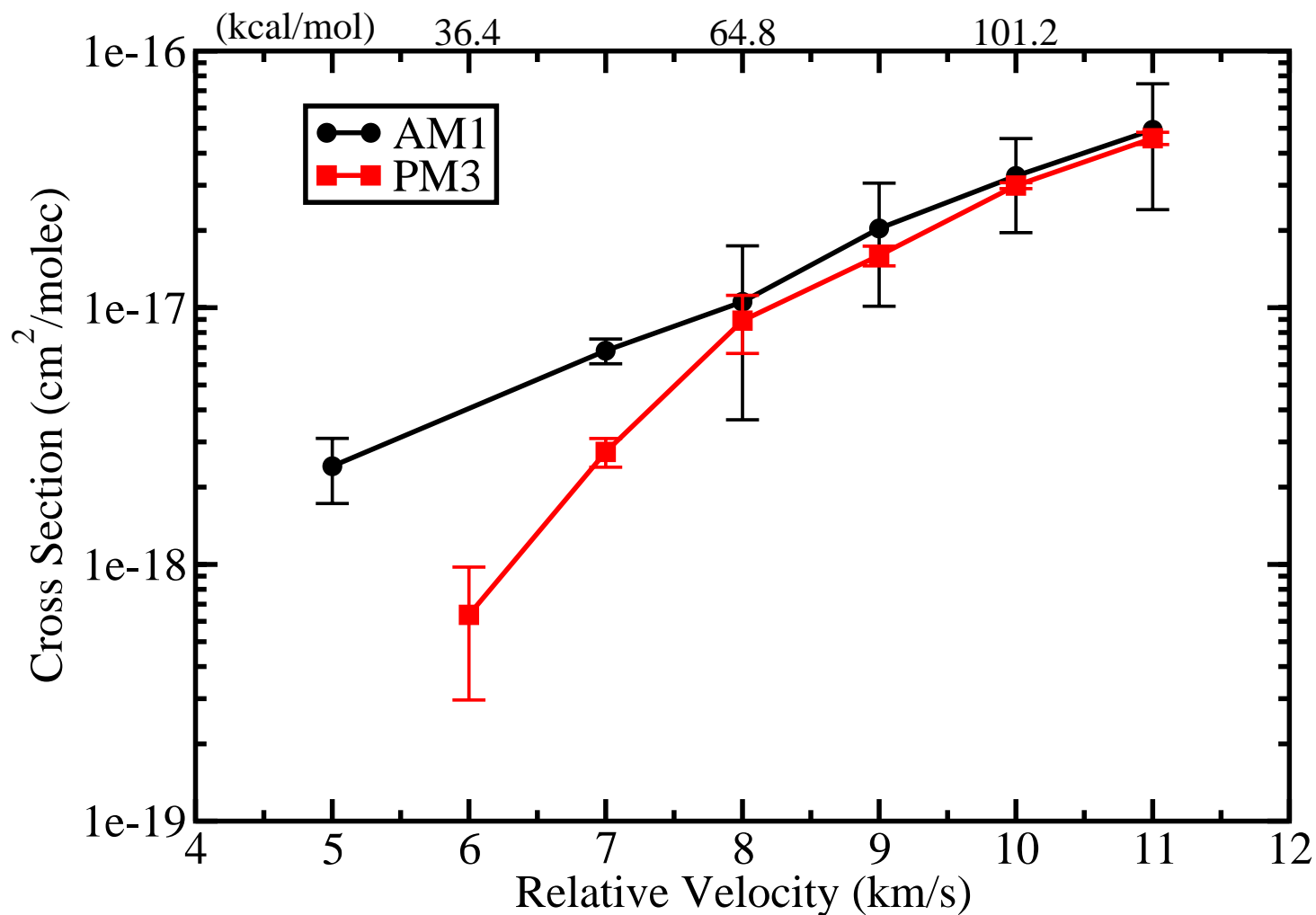
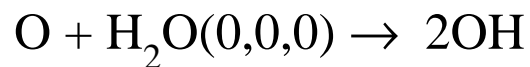
- 1) Excite OH bond in HOD with 4 quanta (about 20 kcal mol<sup>-1</sup> over barrier)
- 2) Let excited HOD react with very low energy (590 cm<sup>-1</sup>) O atom
- 3) LIF detection of product OH and OD

v	OH(v)-DD	OH(v)-Exp.	OD(v)-DD	OD(v)-Exp.
0	0.02		0.97	0.93 ±0.03
1	0.04		0.02	0.07 ±0.03
2	0.32	1.0±0.04	0.00	
3	0.62		0.00	

- Theory yields somewhat hotter distributions than measurements
- Relaxation certainly a factor in experimental set up



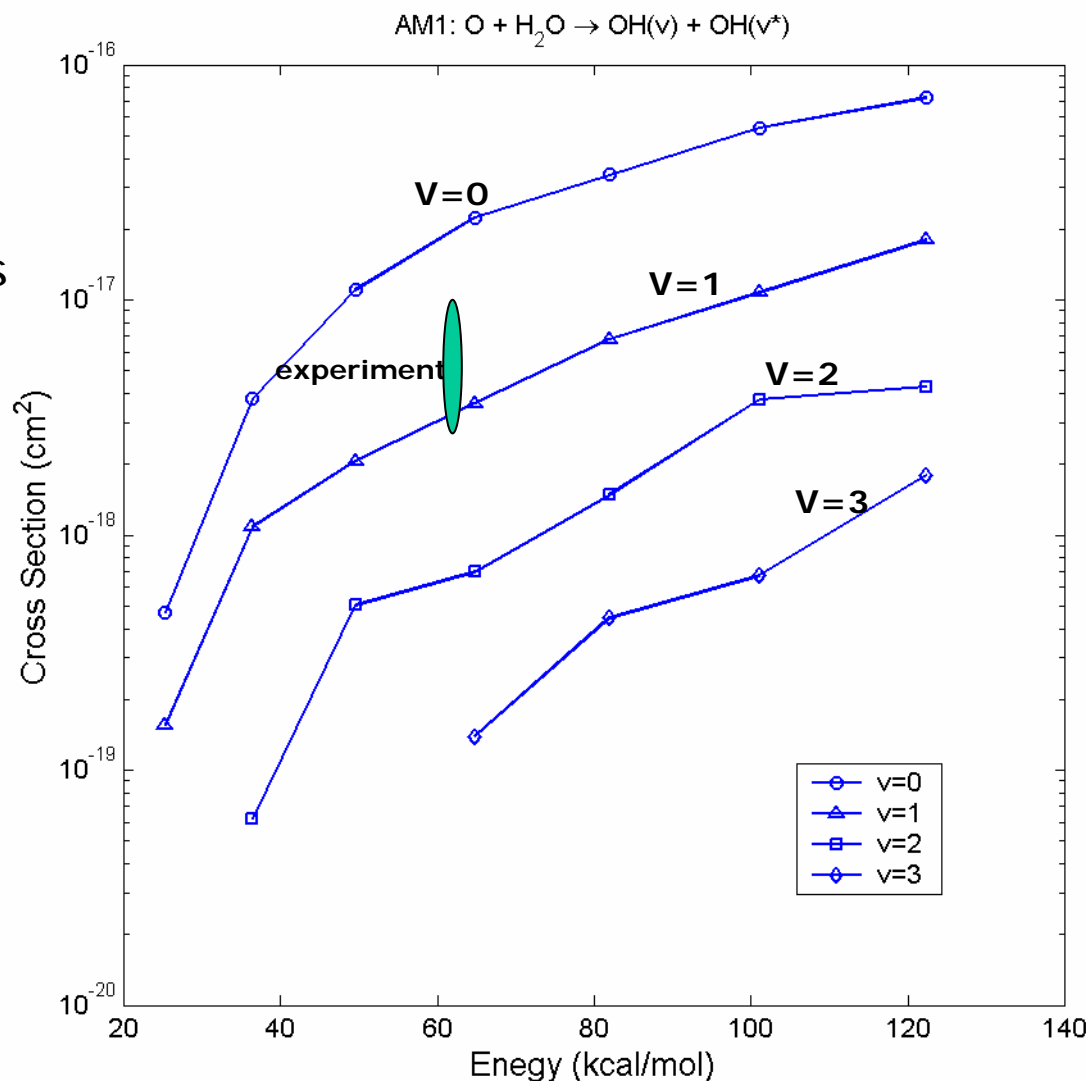
# Consistency of Direct Dynamics Approaches





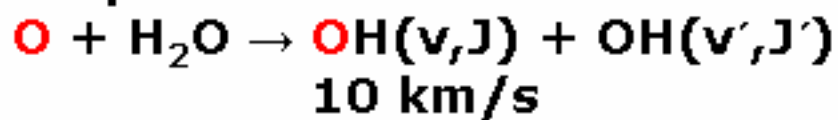
# Direct Dynamics Predictions for OH\* Production

- Direct dynamics cross sections are comparable to experimental measurements at  $\sim 8$  km/s
- Need further analyses, especially spectral comparisons with measurements



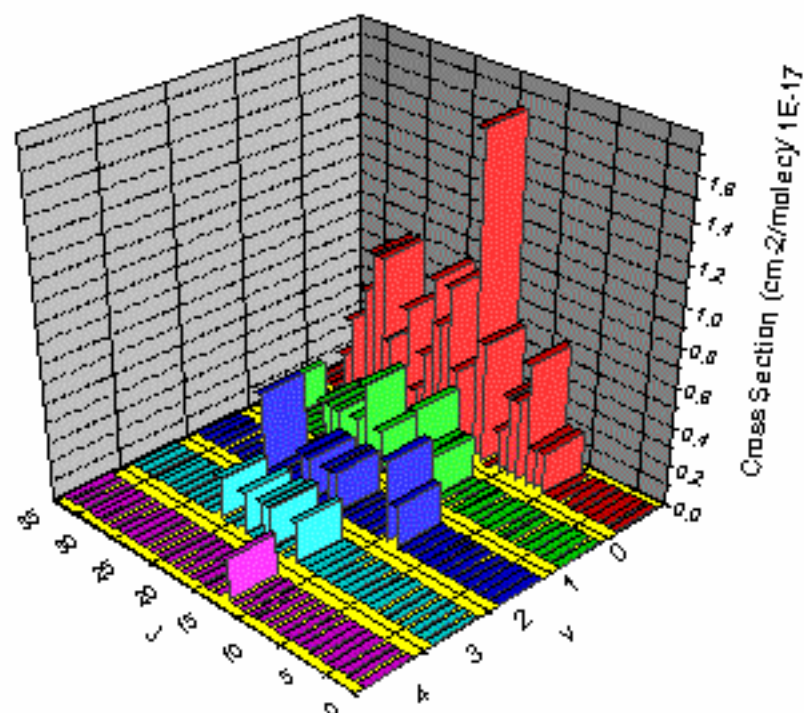


# State Specific Reactive Cross Sections

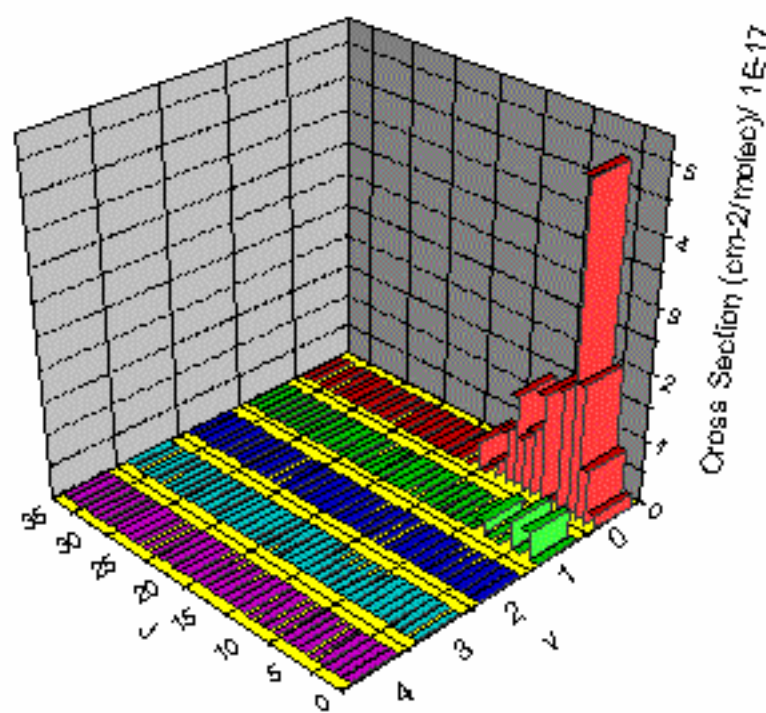


Note that OH products are formed in 'hot' and 'cold' populations

OH( $\nu, J$ )



OH( $\nu, J$ )

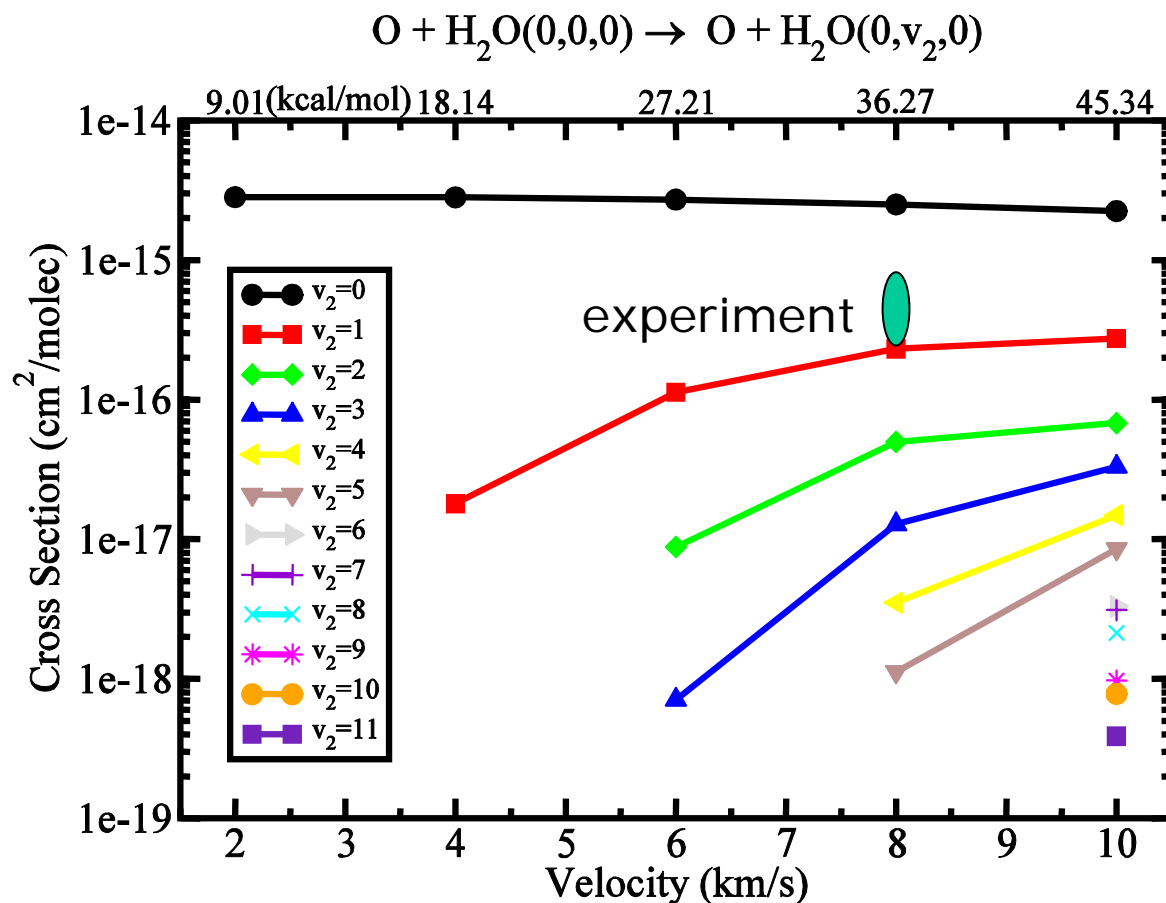




# Direct Dynamics Results for

$$\text{O} + \text{H}_2\text{O} \rightarrow \text{O} + \text{H}_2\text{O}^*$$

- With classical approach, it is not straightforward to determine product vibrational mode
  - Assume most vibrational energy goes into  $\text{H}_2\text{O}(v_2)$
  - Preliminary results are comparable to experiment





# Status of Direct Dynamics Calculations

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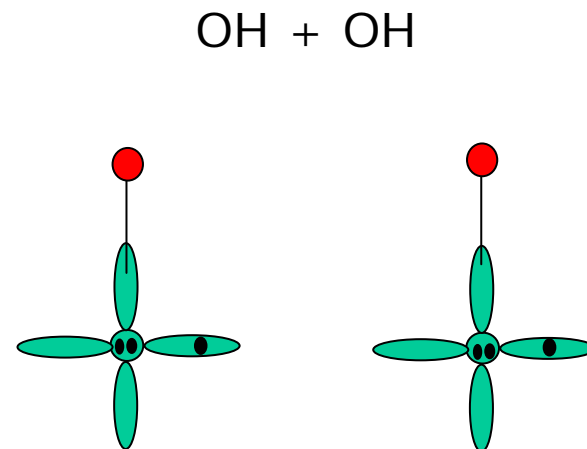
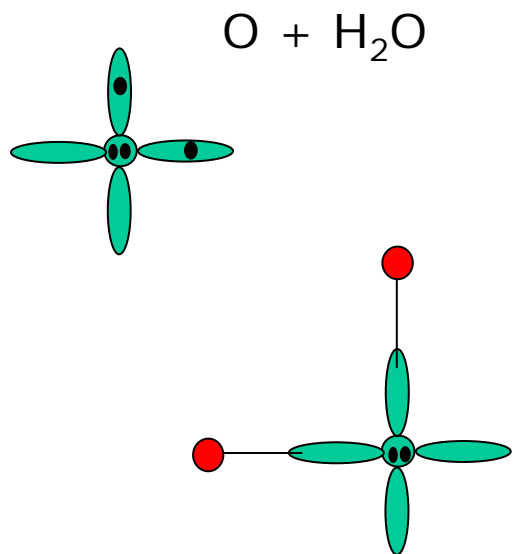


- Investigating possible  $\text{H} + \text{OOH}$  product channel (high energies)
- More calculations for better statistics
- Simulating spectra from final OH distributions
  - Two temperature fit
  - Compare to PSI CVF measurements (OH overtone)
  - Other spectral data
- Continue comparisons with  $\text{HOD}^* + \text{O}$  measurements



# O + H<sub>2</sub>O Potential Energy Surface: Electronic Structure Calculations

- Basis: TZV + 2d,1f on O + 2p on H; 90 total basis functions
- 10e8o CASSCF + MP2 (1s,2s frozen, 2 lone pair, 2 bonding, 2 alpha, 2 anti-bonding)
- No symmetry; 3 state average
- Calculated  $\Delta H = 15.6 \text{ kcal mol}^{-1}$ , exp. =  $14.7 \text{ kcal mol}^{-1}$

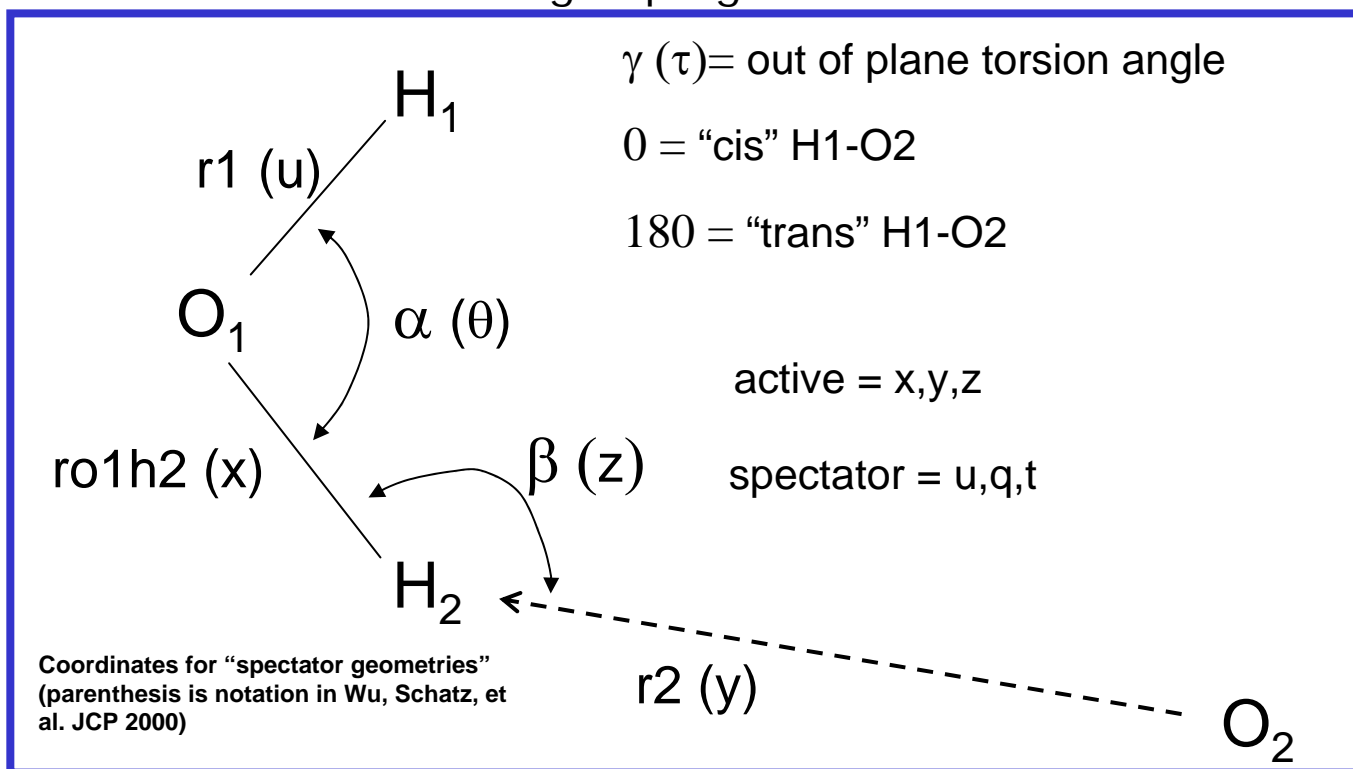






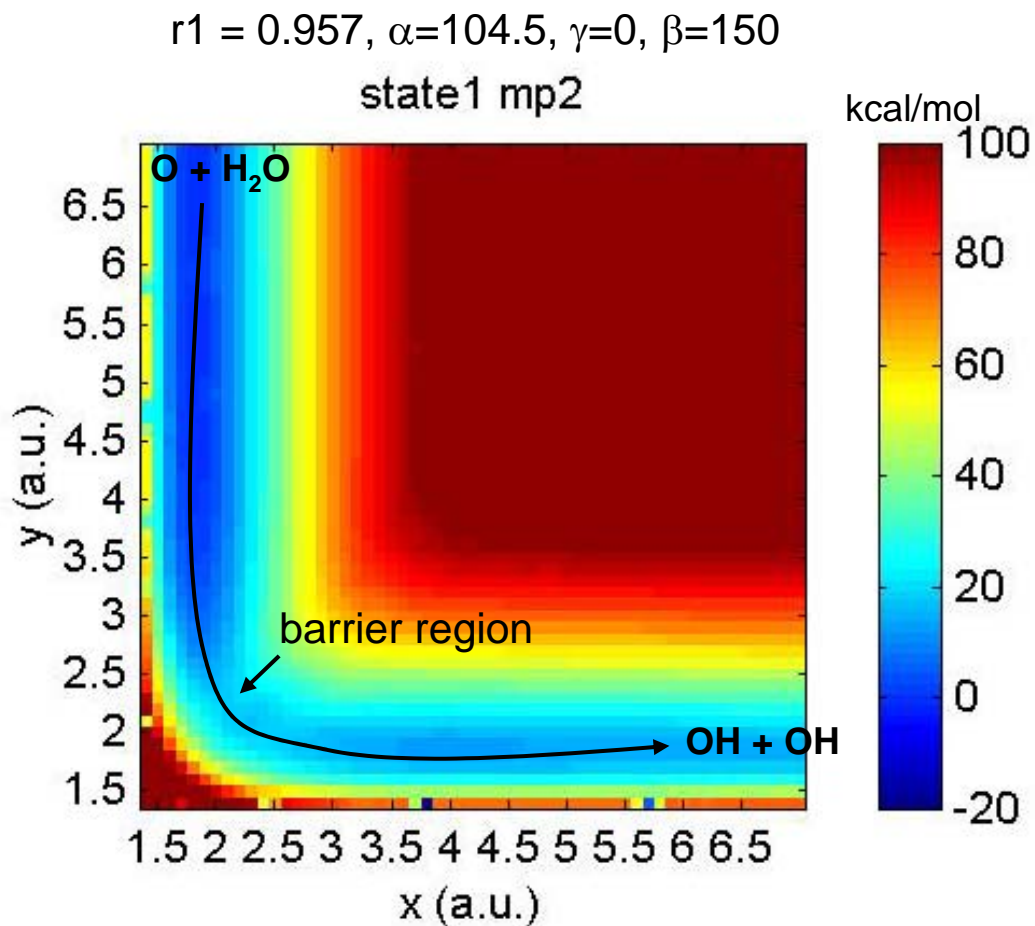
# Internal Coordinates for Electronic Structure Calculations

- As reaction proceeds,  $x$  and  $y$  change
  - For Reagents:  $x$  is small,  $y$  is large
  - For Products:  $x$  is large,  $y$  is small
- Performed  $\sim 1.e5$  fixed point calculations
- Surface fitting code nearly complete,
  - Unit testing in progress



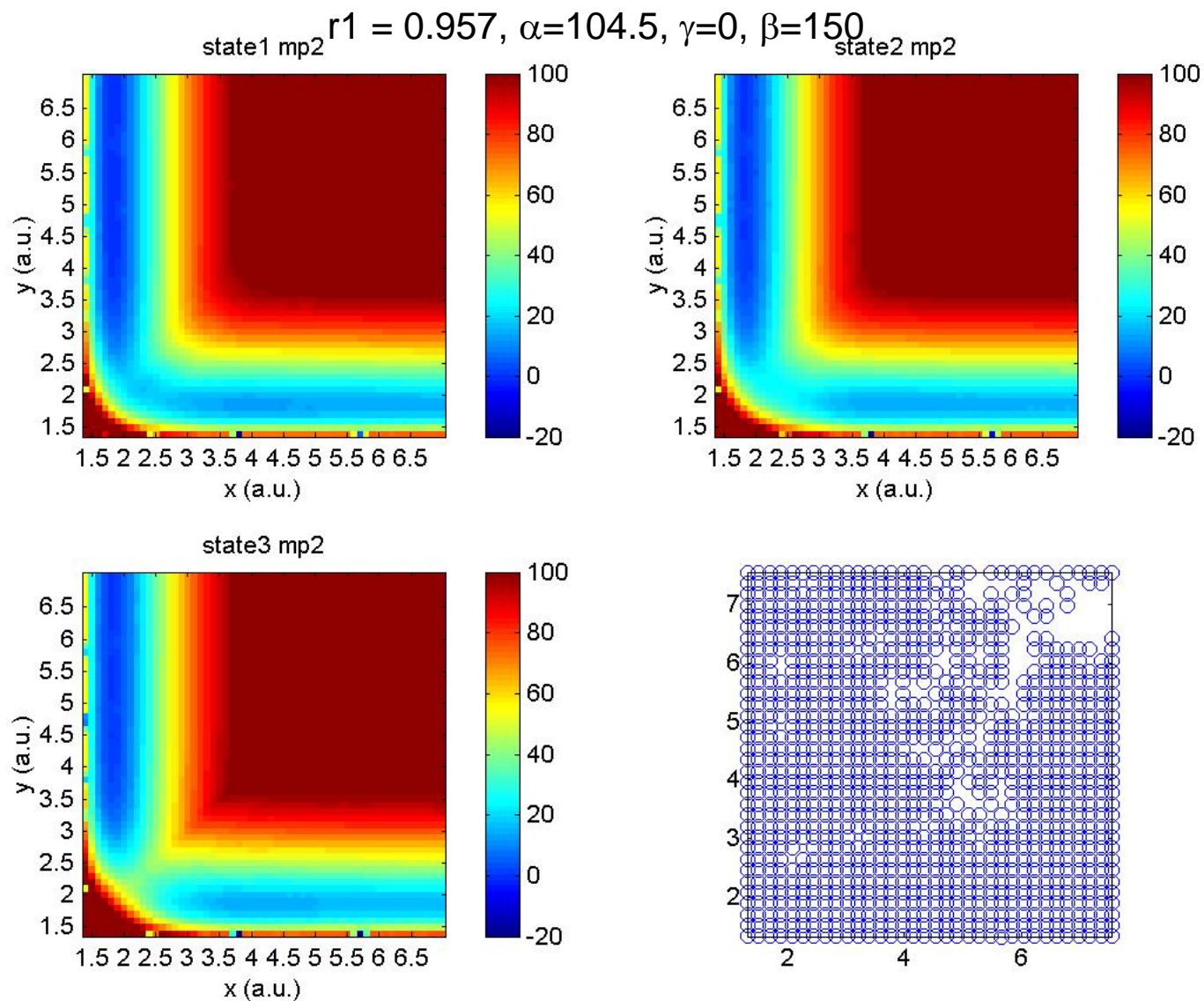


# Electronic Structure Calculations: All Coordinates Fixed Except x and y





# Intend to Follow Lowest Three Electronic States





# Surface Fitting Computation Procedure

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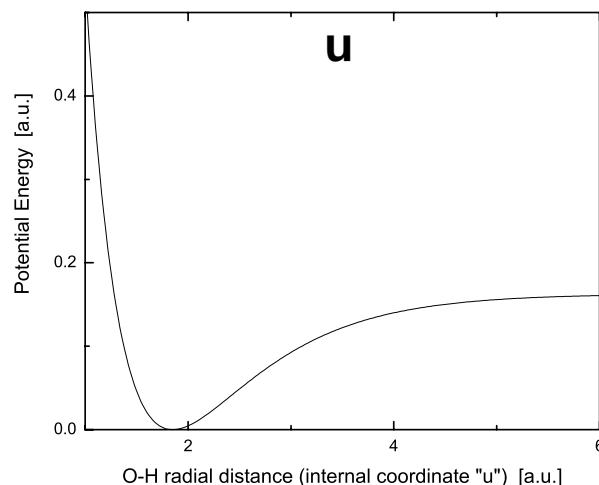
- First, compute electronic energies for selected geometries
- Then, generate a potential-energy surface from data using a combination of pre-determined functional behavior and multidimensional spline interpolation
  - Multi-dimensional spline routines from Princeton Plasma Physics Lab
  - Water and OH potentials from Schwenke et al. [J. Chem. Phys., 1996]
  - Functional fits to least sensitive coordinates from Schatz et al. [J. Chem. Phys., 2000]
- Once complete, the potential corresponding to an arbitrary set of Cartesian coordinates can be computed within a classical dynamics simulation.



# Spectator and Active Coordinates

The twelve Cartesian coordinates of our four-atom system can be uniquely described by a set of six “internal” coordinates. These six coordinates are separated into three “active” coordinates ( $x, y, z$ ), which will be fit using multidimensional splines and three spectator “coordinates” ( $u, \theta, \tau$ ), which will be fit using pre-determined functional forms.

$$V_Q = V_{active}(x, y, z) + V_{spectator}(u, \theta, \tau; x, y, z)$$



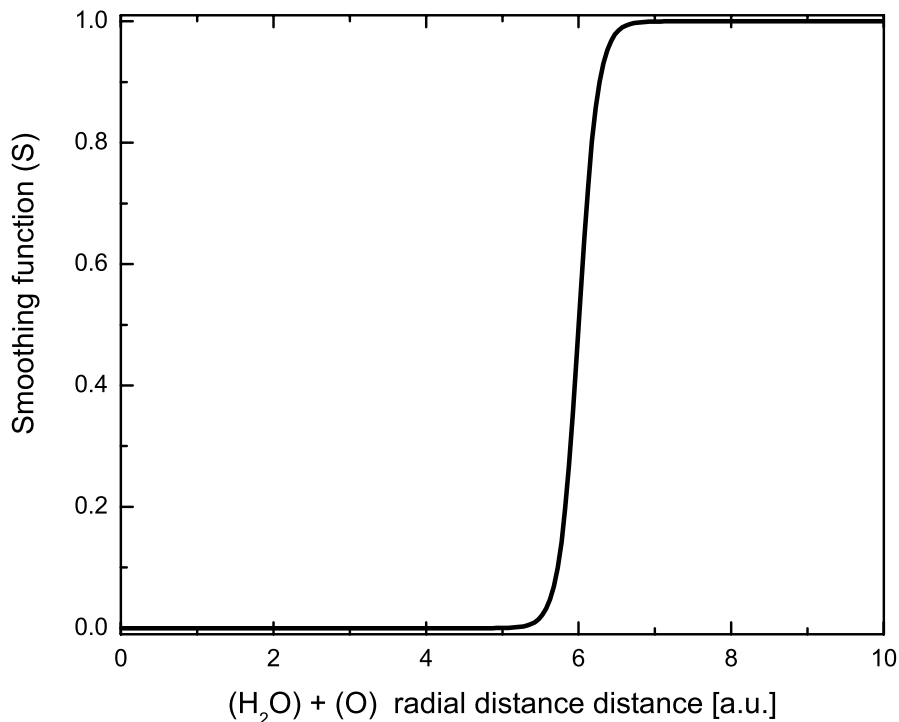


# From Reactants to Products

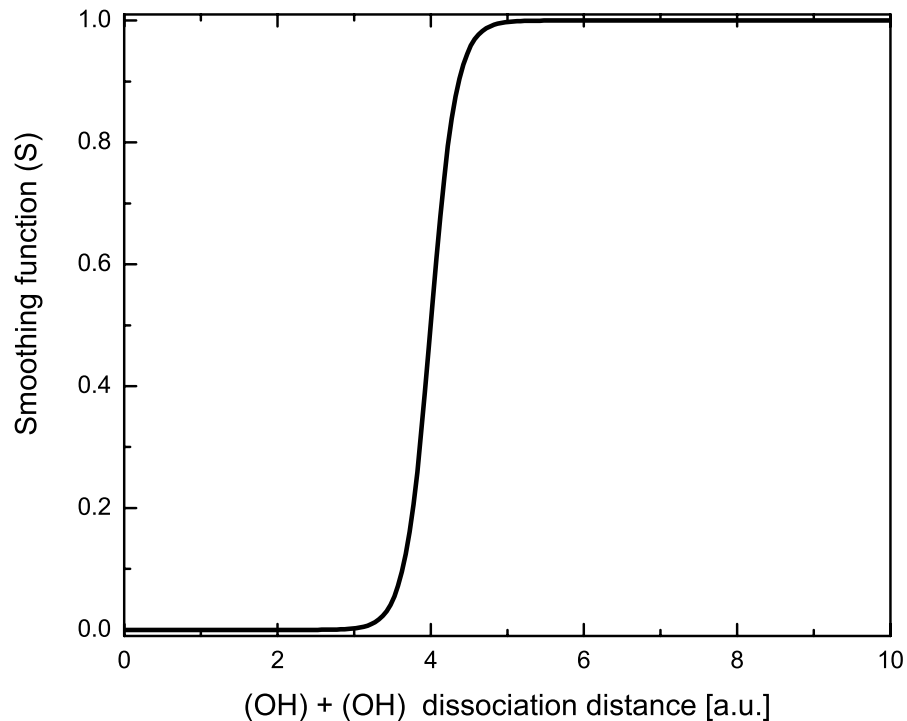
The potential energy surface (“V”) will transition smoothly from the initial reactants state (“R”) to final products state (“P”) using smoothing functions (“S”):

$$V = (1 - S_R - S_P) \cdot V_Q + S_R \cdot V_R + S_P \cdot V_P$$

Reactants State Switching Function



Product State Switching Function

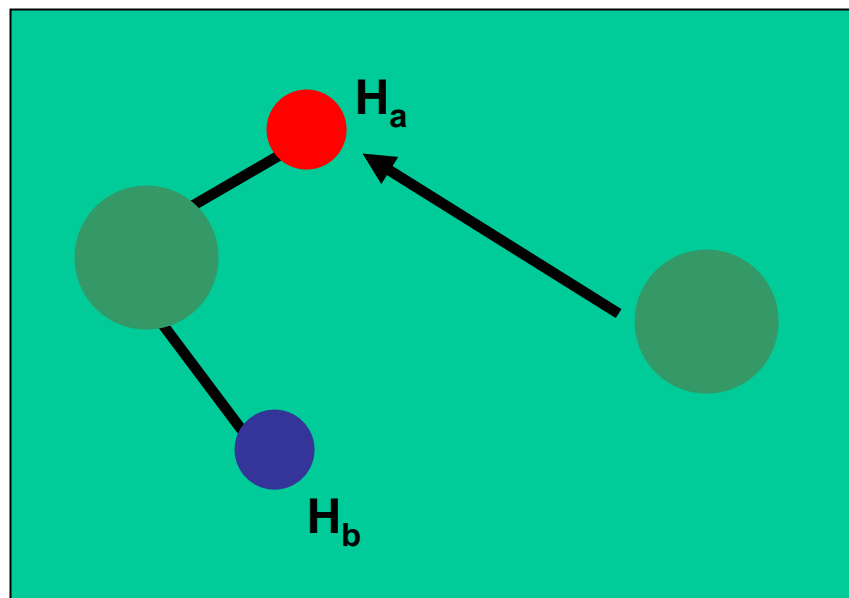
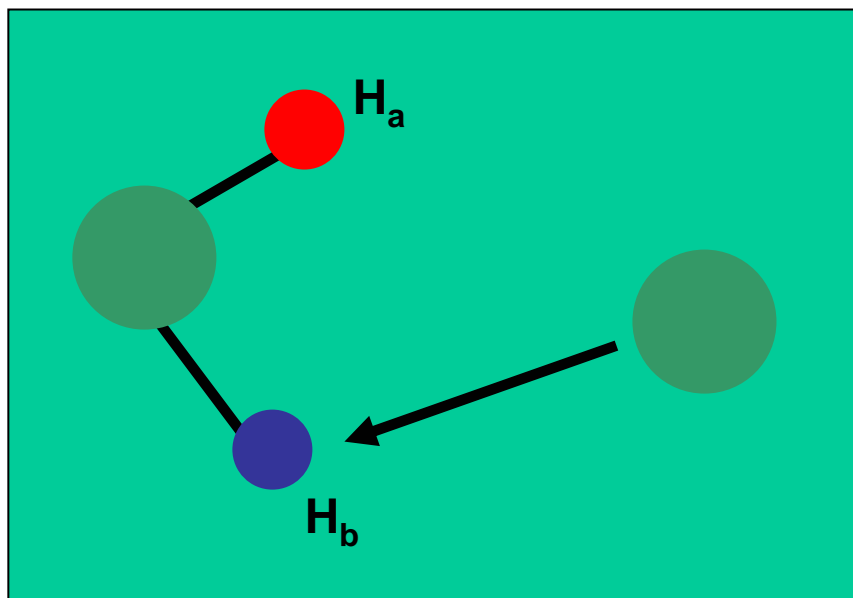




# Potential Symmetrization

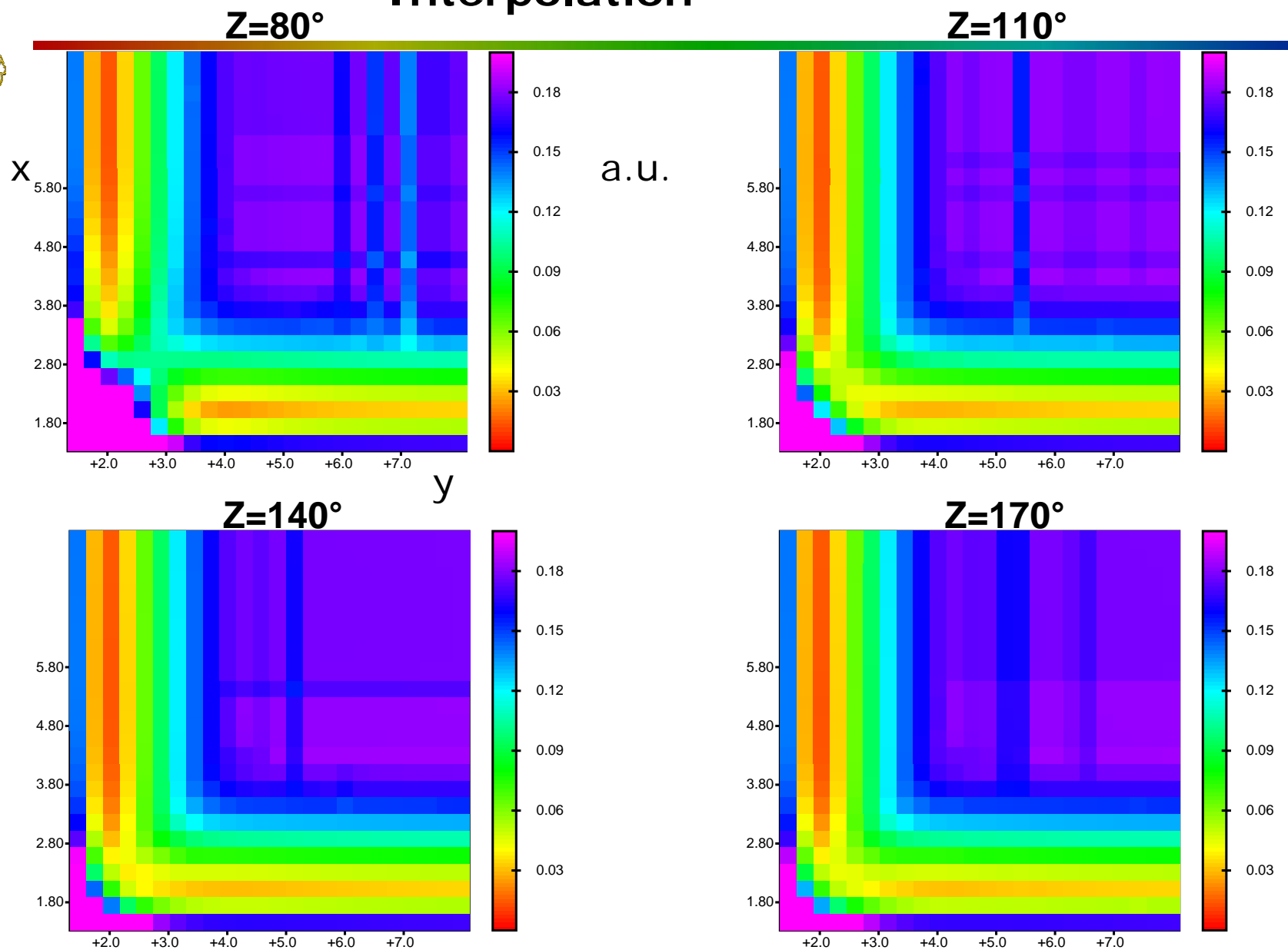
The incoming oxygen atom can bind to either hydrogen atom in the water molecule. To model two possible scenarios using a single set of Cartesian coordinates, a 'symmeterization' procedure is added in which the position of the two hydrogen atoms are transposed. Transitioning between the two orientations is provided by a smoothing function (S).

$$V_{Final} = (1 - S_s) \cdot V((H_a - O_a - H_b) + O_b) + S_s \cdot V((H_b - O_a - H_a) - O_b)$$





# Interim Fitting Results – Spline fit with Interpolation





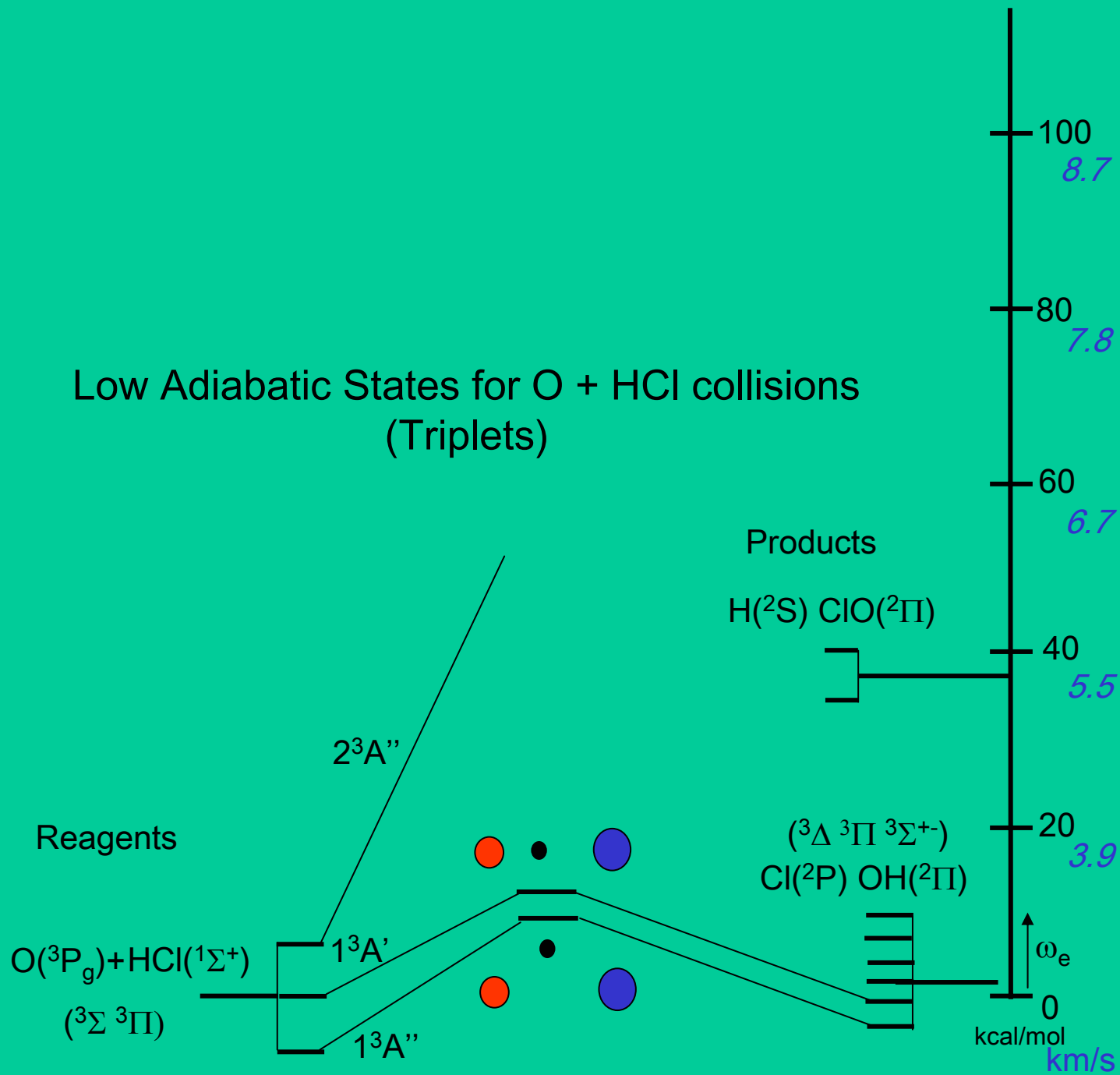


# Overview of O + HCl System

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- Many important studies, but very little information at high velocities
  - major channels  $O + HCl \rightarrow O + HCl^*, Cl + OH^*$
- Experimental Studies:
  - Numerous experimental studies of the rate constant up to  $\sim 2500$  K
  - Final state resolved measurement of  $O + HCl^*$
- Theory
  - Large body of work over many years up to the present
    - Detailed, high level potential energy surfaces (PES)
    - Classical and Quantum studies (rate constant)
    - Very recent study (PES+dynamics):
      - » *Ramachandran (Louisiana Tech), Peterson, Bowman*
  - **Note: H + OCl channel missing in all studies**
- No clear picture of magnitude or relative importance of channels

# Low Adiabatic States for O + HCl collisions (Triplets)





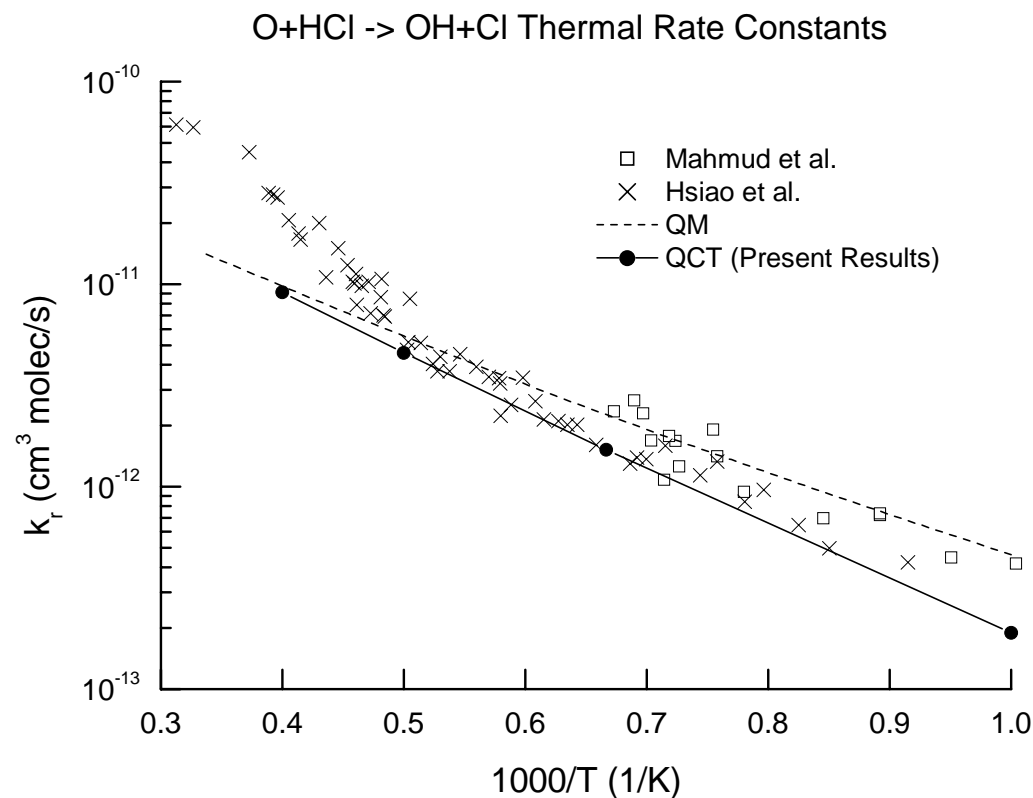
# O + HCl Reaction Approach

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- Perform classical dynamics calculations
  - Use latest surfaces provided by Professor B. “Ramu” Ramachandran (Louisiana Tech)
  - Generate temperature dependent rate constants to compare with available experimental data
  - Generate velocity dependent, state-specific cross sections
  - Analyze final state distributions
- Collaboration with Ramachandran/Bowman groups
  - Quantum/classical dynamics study



# Thermal Rate Constant for O+HCl Reaction



- Good agreement between present calculations (QCT) and experiment/QM results for  $T < 2000\text{K}$

-Possible quantum (tunneling) effects  
< 1500 K

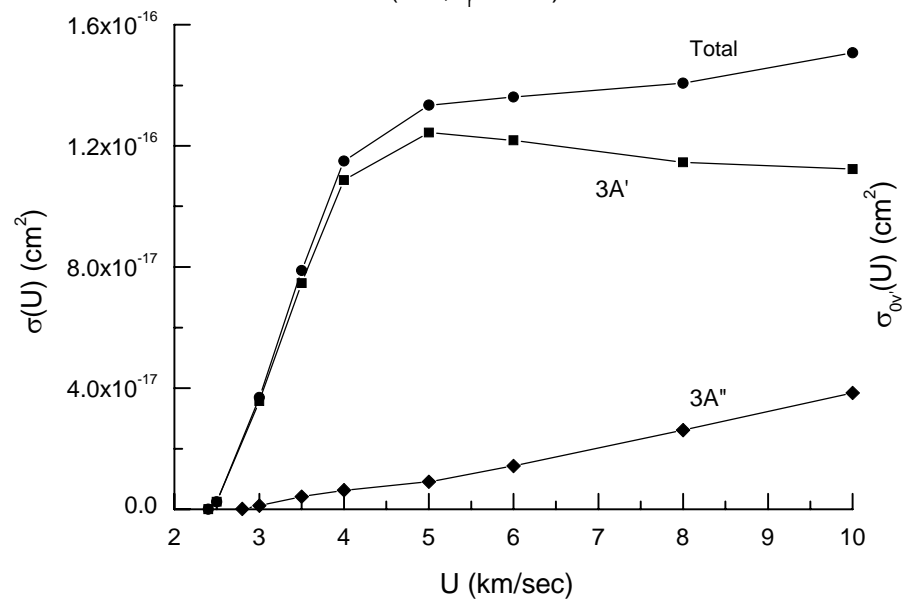
- Disagreement between theory and experiment for  $T > 2000\text{K}$  is not currently understood

– O(<sup>1</sup>D) contamination  
– OCl channel accessible

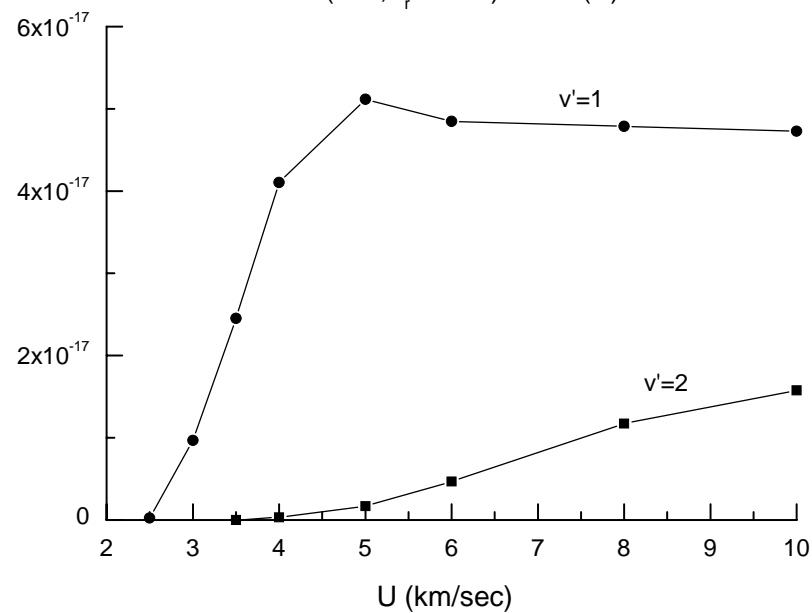


# Velocity Dependence of O+HCl Reaction

O+HCl( $v=0$ ,  $T_r=300\text{K}$ )  $\rightarrow$  OH+Cl

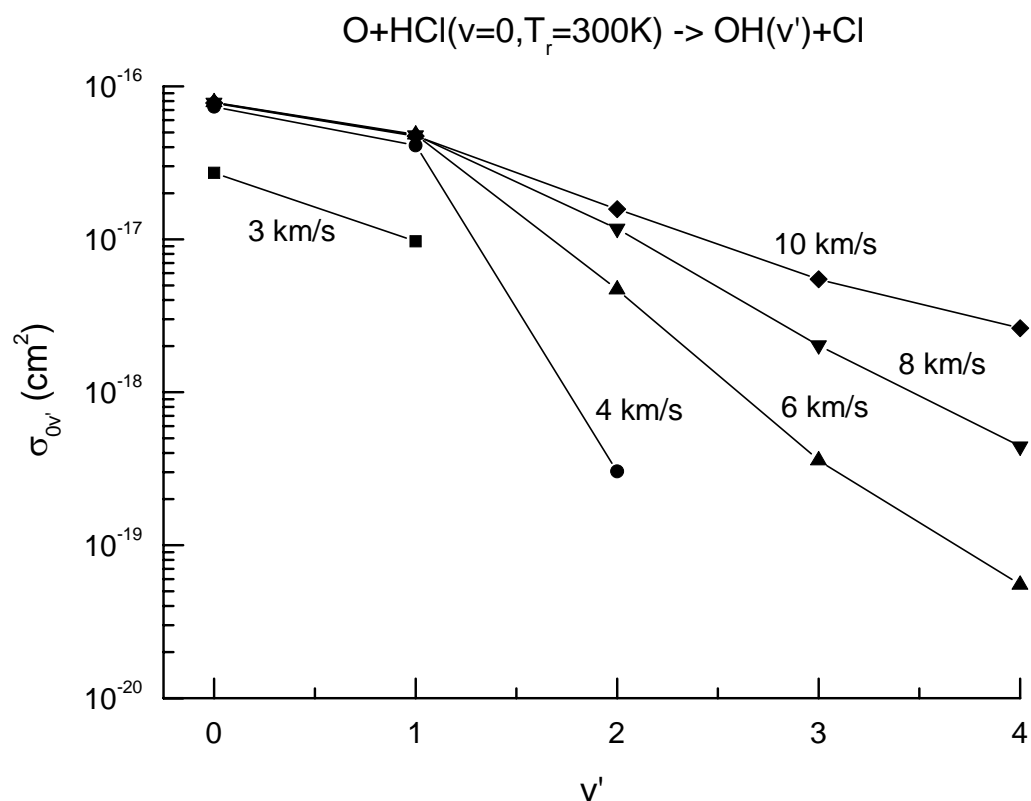


O+HCl( $v=0$ ,  $T_r=300\text{K}$ )  $\rightarrow$  OH( $v'$ )+Cl





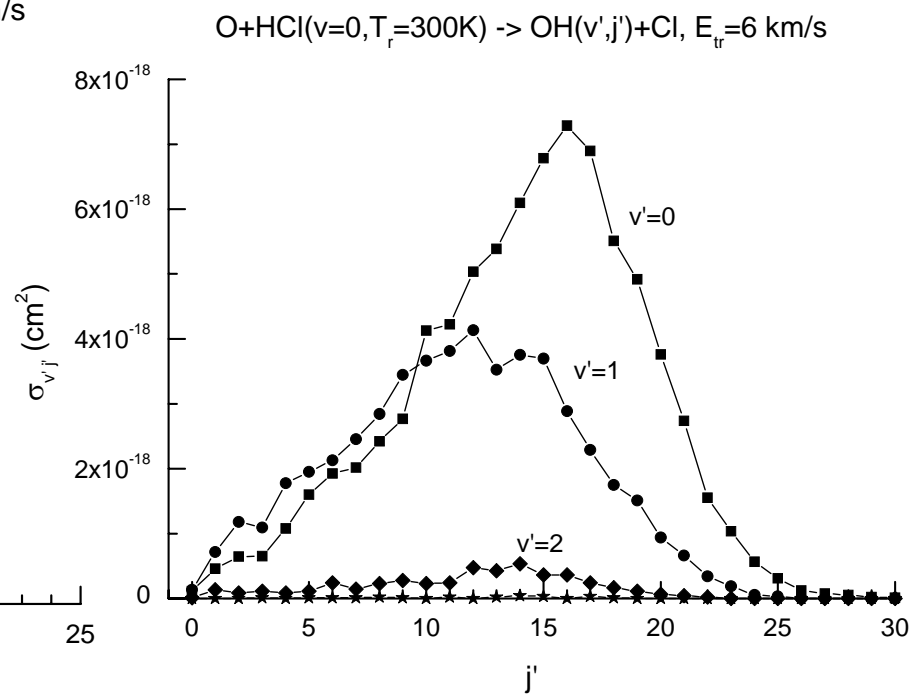
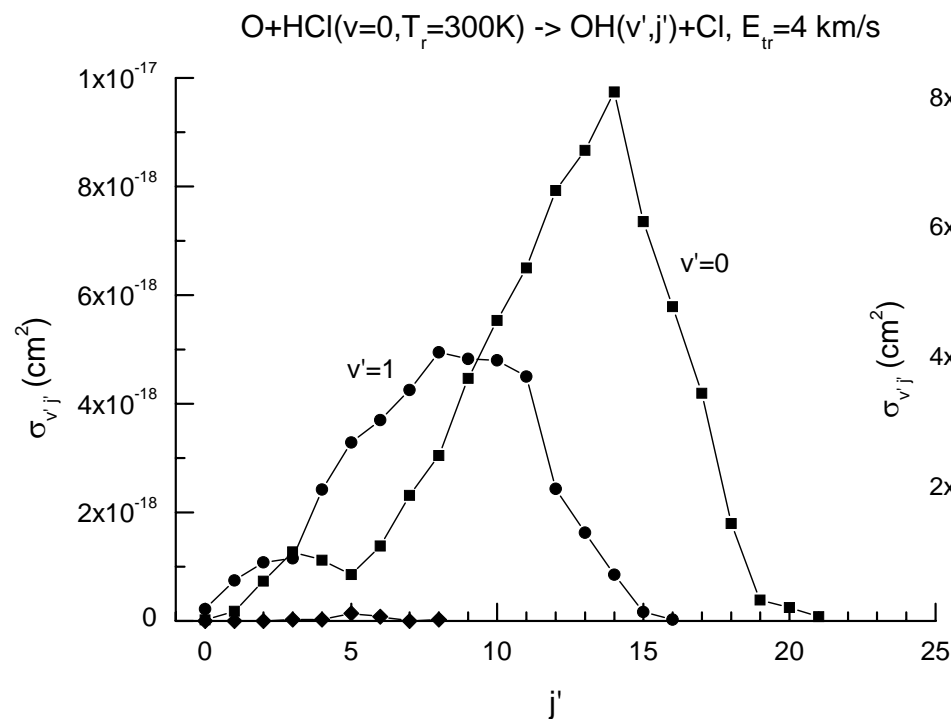
# Velocity Dependence of OH Vibrational Distributions



- Exponential falloff of vibrational distributions consistent with Polanyi studies of the effect of barrier location of vibrational energy in products
  - Late barriers (in product channel) result in mixed energy release into translation & rotation



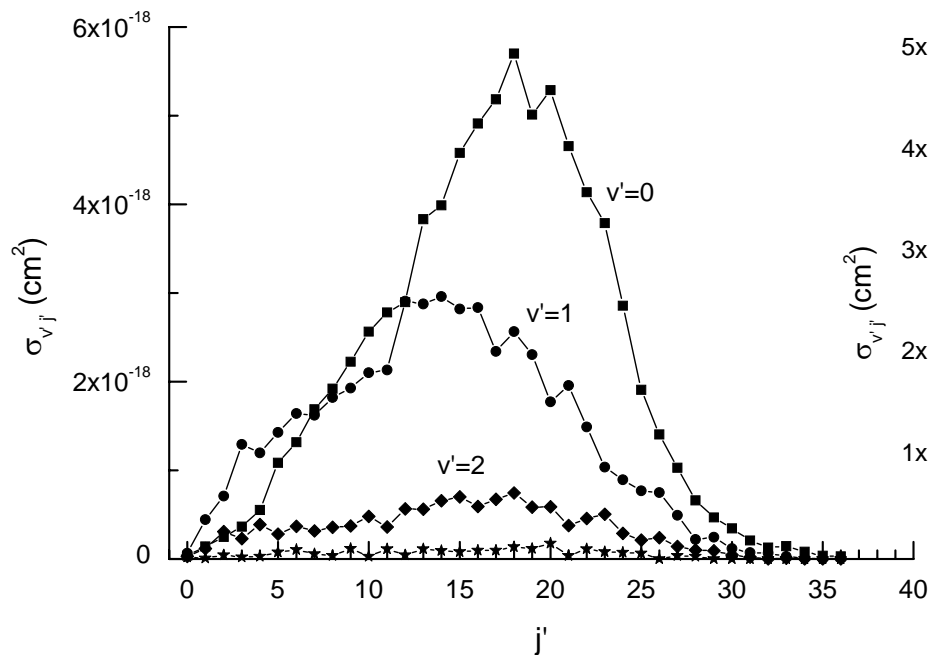
# Velocity Dependence of OH Vibrational/Rotational Distributions



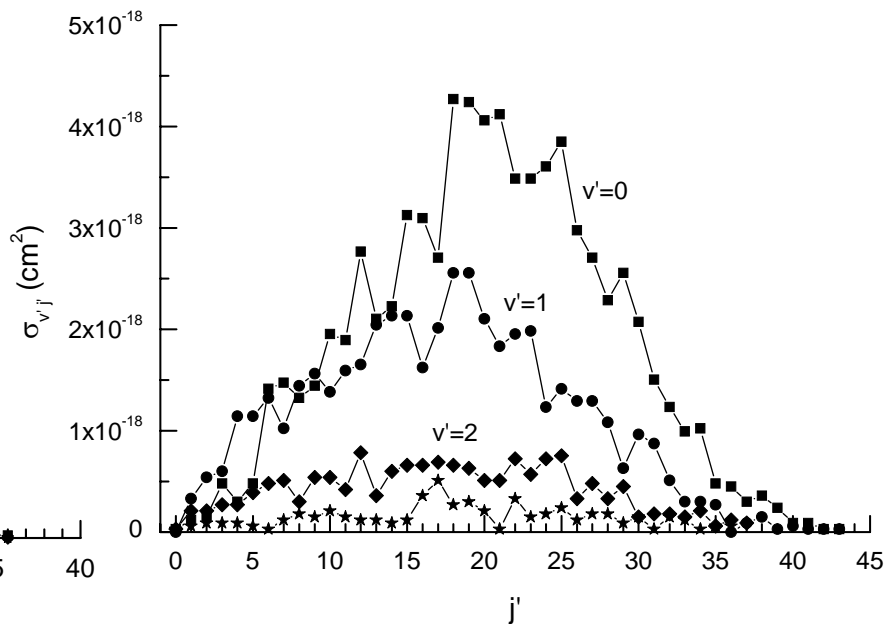


# Velocity Dependence of OH Vibrational/Rotational Distributions

$\text{O} + \text{HCl}(v=0, T_r=300\text{K}) \rightarrow \text{OH}(v', j') + \text{Cl}, E_{tr}=8 \text{ km/s}$



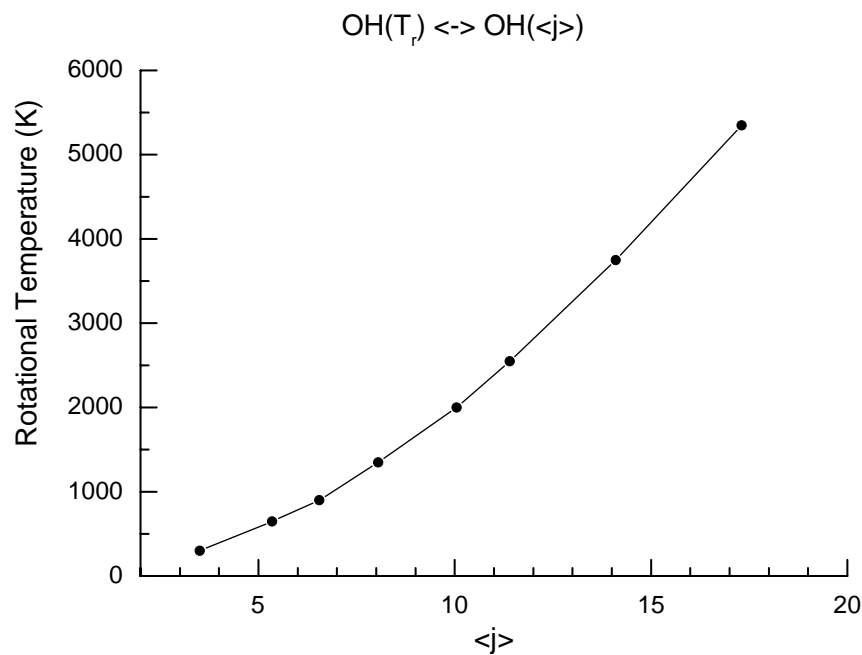
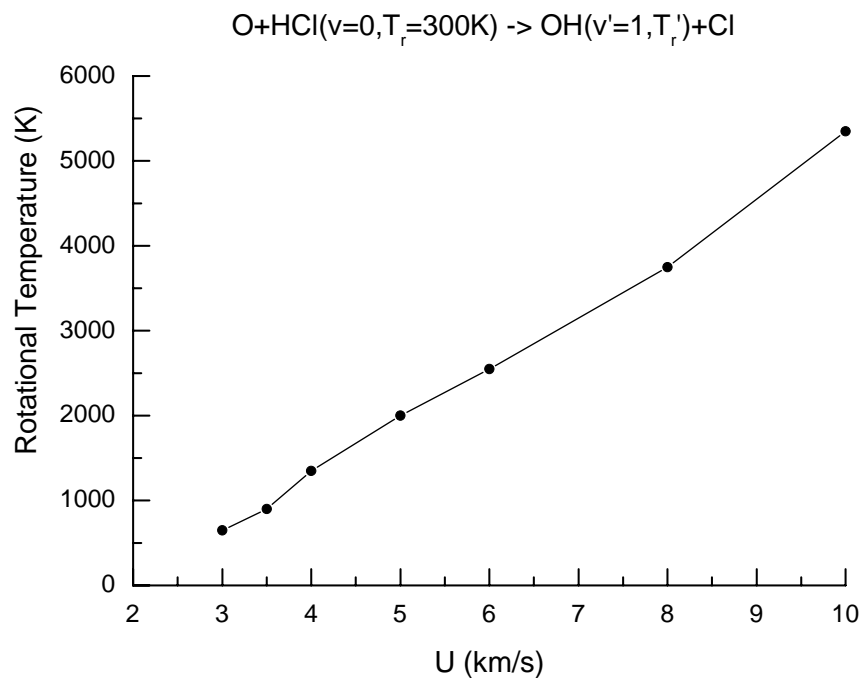
$\text{O} + \text{HCl}(v=0, T_r=300\text{K}) \rightarrow \text{OH}(v', j') + \text{Cl}, E_{tr}=10 \text{ km/s}$





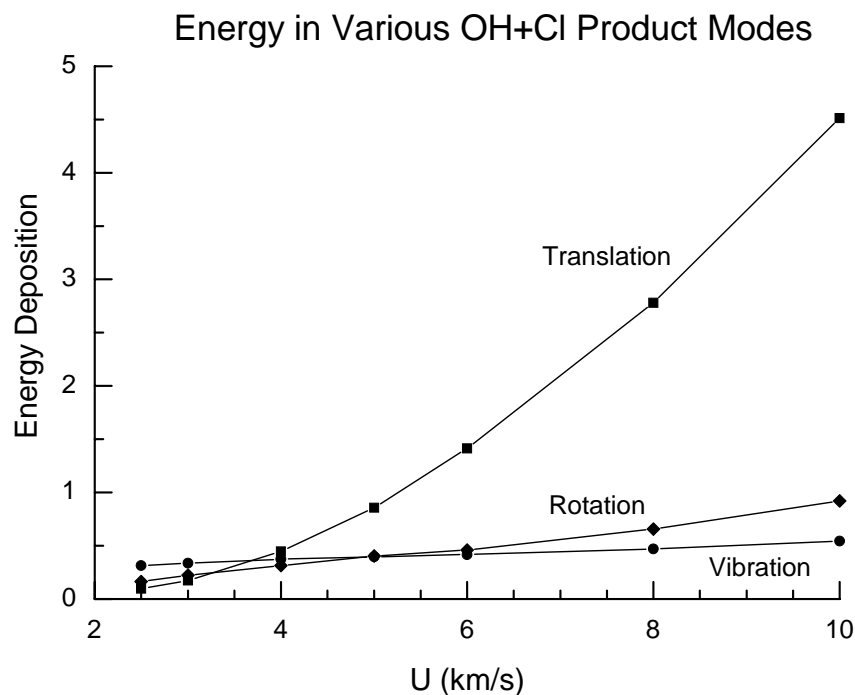
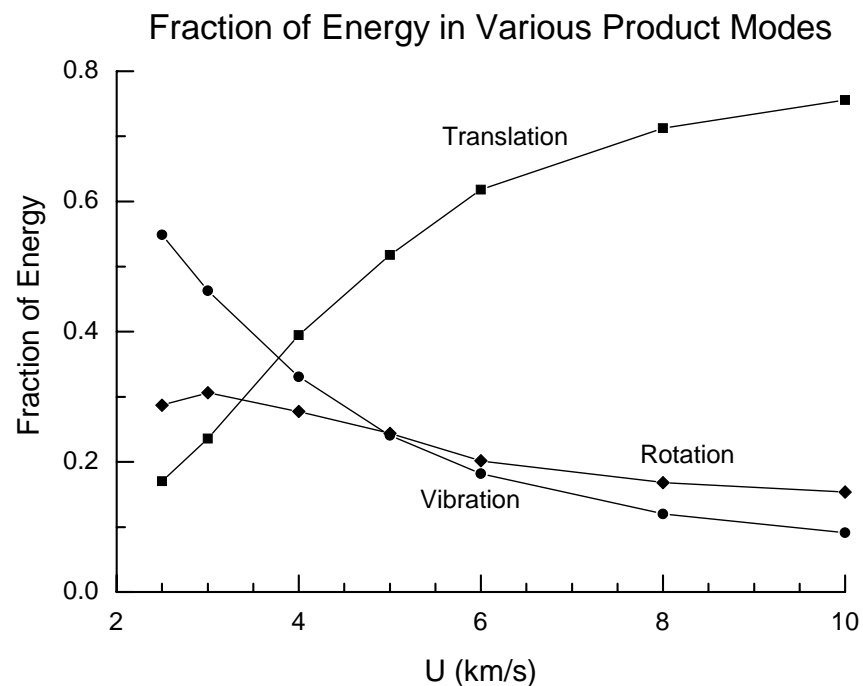


# Estimate of OH( $v'=1$ ) Rotational Temperatures



Based on 1<sup>st</sup> moment of rotational distributions (assuming a Boltzmann distribution of OH( $v'=1, j$ )), OH rotational temperatures approach 6000K

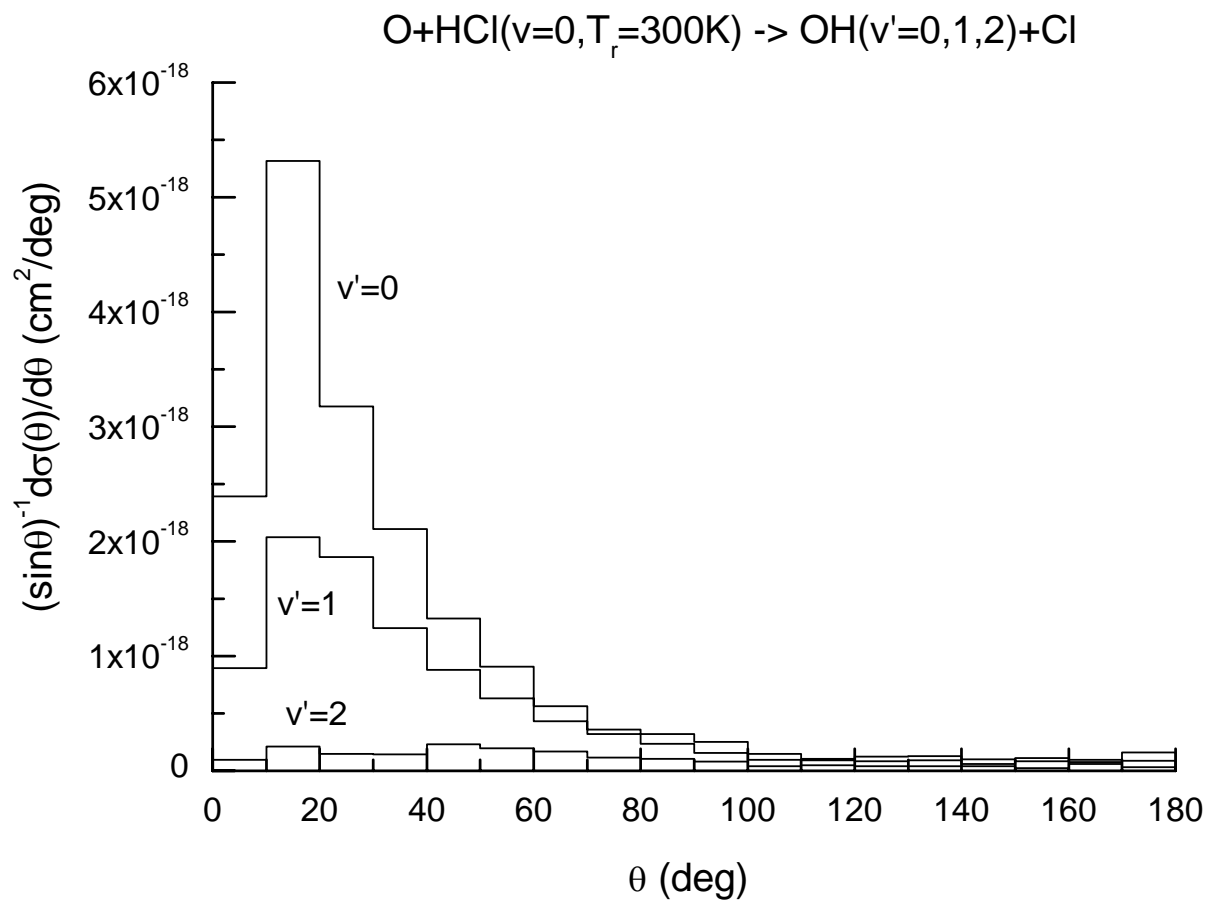
# Energy Deposition in O+HCl Reaction



- Reactant translational energy is preferentially channeled into product translational energy
- Rotational excitation is substantial for  $U > 4$  km/s

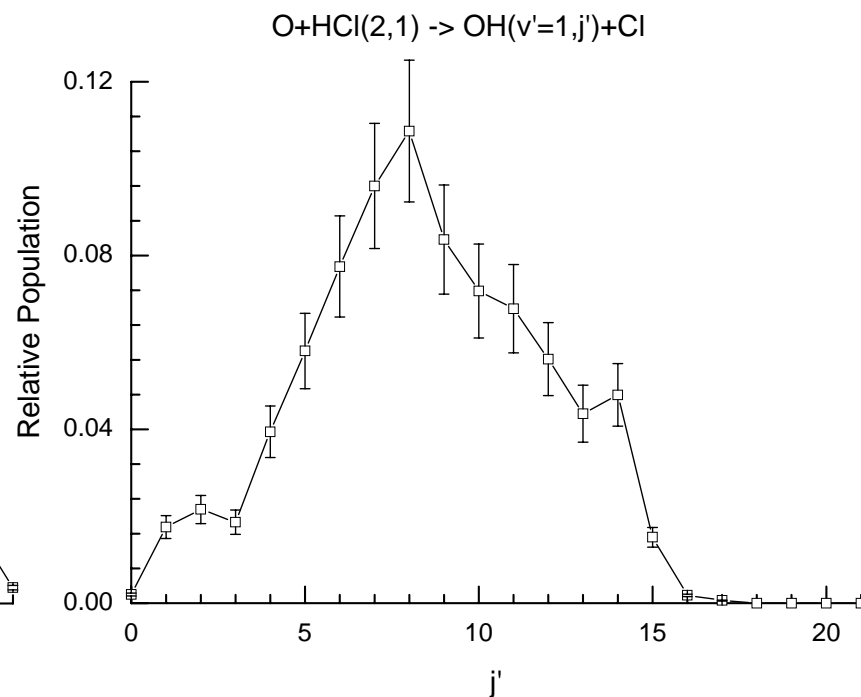
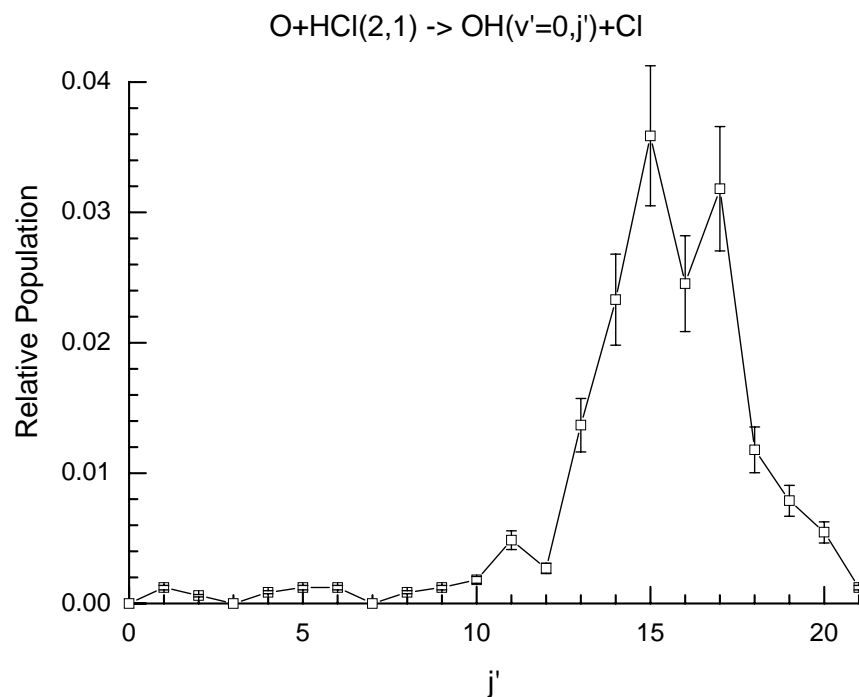


# OH Differential Cross Section at 8 km/s





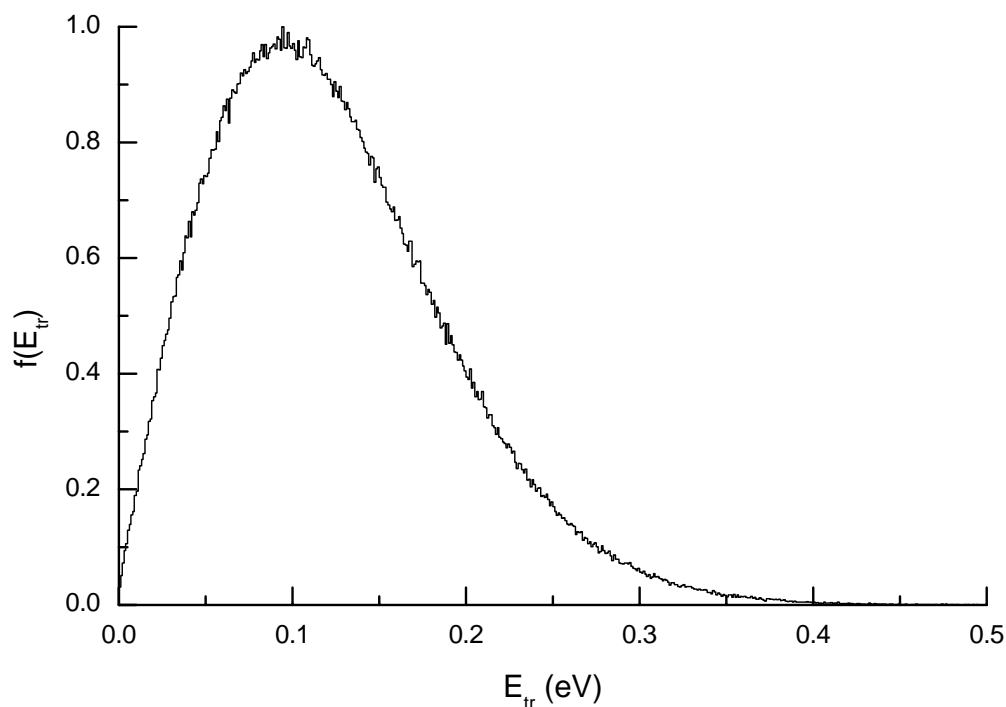
# OH( $v'=0,1;j'$ ) Rotational Distributions (Averaged over Experimental $E_{tr}$ Distribution)





# O+HCL Energy Distribution

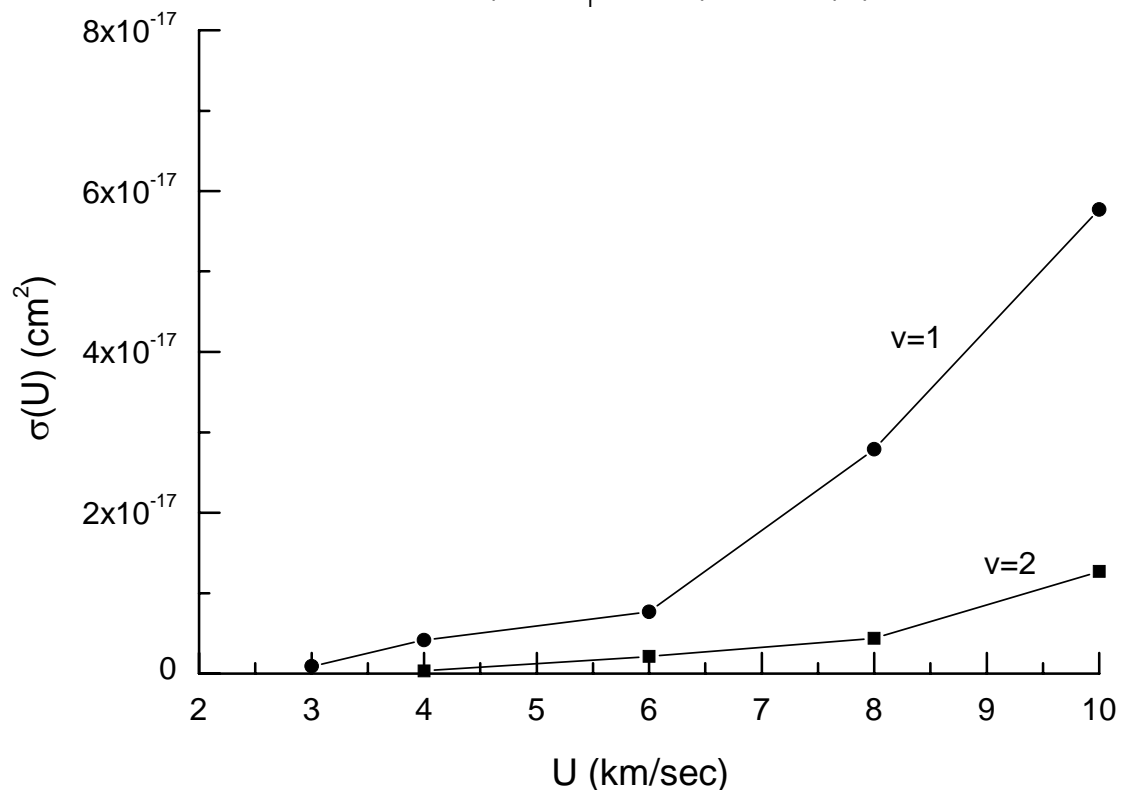
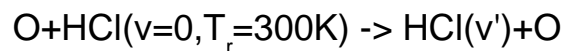
O+HCL Translational Energy Distribution



- Experimental velocity distribution of Hradil et al. is fit to sum of Gaussians
- Velocity distribution is first convolved with thermal motion of  $\text{NO}_2$  precursor and then with thermal motion of HCl [van der Zande et al., 1991; Brouard et al., 1992]
- Figure shows resultant O+HCL relative energy distribution generated by trajectory code



# HCl Vibrational Excitation



• Rotational excitation is estimated to be 5000K-8000K in the 6-10 km/s velocity range